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CELLULOSE AND CELLULOSE DERIVATIVES

Second Completely Revised and Augmented Edition

Prepared under the Editorship of

EMIL OTT **HAROLD M. SPURLIN**

MILDRED W. GRAFFLIN

Research Department, Hercules Powder Company
Wilmington, Delaware

PART II

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CELLULOSE
AND CELLULOSE DERIVATIVES

Part II

Chapter VI

PREPARATION OF CELLULOSE FROM ITS NATURAL SOURCES

A. WOOD PULP[1]

WALTER F. HOLZER

The commercial pulping of wood as it is known today is based on processes less than one hundred years old. Watt and Burgess[2] in 1854 patented the pulping of wood in hot aqueous sodium hydroxide solutions under pressure. From the cooking chemical the name "soda" process is derived. Tilghman[3] was granted a patent in 1867 on his discovery that wood is pulped in aqueous sulfur dioxide solutions in which part of the sulfur dioxide is combined with calcium as the bisulfite. The sulfite process produces a white pulp, and once the corrosive behavior of the cooking chemicals was overcome, it became for several decades the leading method for preparing pulp. Dahl[4] obtained a patent in 1889 on a modification of the soda process in which sodium sulfate replaced sodium carbonate as make-up in the recovery of cooking chemicals. The sulfate is reduced to sulfide when the organic material in the spent liquor is burned. This pulping process has been called "sulfate" from the make-up chemical, or "kraft" from the German word meaning "strength" in recognition of the strength of its paper products. Because it is less critical of wood species, because of the strength of its products, and because of the advantages of chemical recovery, the kraft process has displaced sulfite by a wide margin in amount of pulp produced. Many other methods have been proposed for pulping wood, but

---

[1] In this section has been incorporated pertinent material from C. M. Koon's section on "Wood Pulp" which appeared (pp. 475–518) in the original edition of this book.

[2] C. Watt and H. Burgess, U. S. Patents 1448 and 1449 (1854); E. Hägglund, *Chemistry of Wood*, 3d ed., Academic Press, New York, 1951, p. 414.

[3] B. C. Tilghman, U. S. Patent 70,485 (Nov. 5, 1867); J. D. Rue, *Paper Trade J.*, **81,** 54 (Oct. 15, 1925).

[4] W. O. Hisey, in L. E. Wise, editor, *Wood Chemistry*, Reinhold, New York, 1944, p. 716.

TABLE 1

Total United States Production of Wood Pulp (U. S. Bureau of the Census)
As compiled for *Pulp and Paper;* reported in tons of 2000 lb.

Year	Total	Sulfite	Kraft	Groundwood	Soda	All Other
1925	3,962,217	1,403,086	409,768	1,612,019	472,647	64,697
1930	4,630,308	1,567,063	949,513	1,560,221	474,230	79,281
1935	4,925,669	1,579,567	1,467,749	1,355,819	417,724	104,810
1940	8,959,559	2,607,789	3,747,992	1,632,727	532,387	438,664
1945	10,167,200	2,359,731	4,471,875	1,826,750	429,757	1,079,087
1950	14,827,152	2,855,825	7,508,376	2,220,795	522,990	1,719,166

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VOLUME V

Cellulose and Cellulose Derivatives

Second Completely Revised and Augmented Edition

Edited by
Emil Ott and Harold M. Spurlin, *Coeditors*
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Part II

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few have developed beyond the laboratory stage, and only one, the neutral sulfite process, in which a liquor containing sodium sulfite and sodium bicarbonate is used, has achieved any commercial importance.

Softwoods or conifers (gymnosperms) are by far the more important type of trees in pulping and subsequent papermaking because of their longer fibers (about 3–4 mm.). Hardwoods or deciduous trees (angiosperms) with their shorter finer fibers (1 mm.) are used in special applications where paper properties such as surface smoothness or softness are of value. In some areas where softwoods are becoming scarce, or to achieve better balance in the use of the wood, the utilization of hardwoods is increasing, especially through application of the neutral sulfite process.

The size of the pulp industry and its growth in the last quarter of a century are illustrated in Table 1.[5] The production of pulp in 1950 was over three and one-half times that in 1925. In that period the production of soda pulp remained static, close to the 500,000-ton level. Groundwood (a pulp produced mechanically by defibering wood on a grindstone) increased less than 40%. Sulfite production doubled. The miscellaneous small processes (mostly high-yield pulps for paperboard and wallboard) increased from almost nothing to 1,700,000 tons. The most phenomenal growth was in kraft which started the period with a production of only 400,000 tons or 10% of the total, and ended it with 7,500,000 tons or a little over 50% of the total.

1. General Considerations

(a) COMPOSITION OF WOOD AND PULP

The composition of a softwood and of a hardwood in terms significant in pulping are diagrammed in Figure 1A. The values given are considered generally typical. Cellulose is the alpha fraction of a holocellulose residue. This fraction usually constitutes slightly over half the total wood substance, and hardwoods are generally richer in it than are softwoods. Hemicelluloses comprise the balance of the carbohydrate fraction and usually amount to about 20%. Softwoods contain just under this figure, and hardwoods just over. A typical lignin content of a softwood is 28% with a range of 25–32%. The same fraction of a hardwood is 22% with a range of about 18–24%. The extractives, including resins, gums, fats, waxes, and coloring matters, will average 2–3%, but, of course, vary widely with the species.

The sulfite or the kraft process will produce a pulp suitable for average papermaking in about 45% yield based on the original wood. This yield is represented by the block graph in Figure 1B. On the basis of the pulp, the cellulose fraction now amounts typically to 85%, the hemicelluloses to 11%, the lignin to 3%, and the extractives to 1% or less. These fractions will vary from softwood to hardwood pulps in about the same way that they did in the woods. Cooking has altered the properties and composition of all fractions. The degree of polymerization (D.P.) of the cellulose has been lowered and has been widened in range. The nonresistant hemicelluloses have been largely removed along with some of the resistant ones, and the hemicellulose fraction now consists of the balance of the resistant hemicelluloses and degradation products of cellulose. The amount will vary on either side of the figure given as much as 4%, depending on the wood species and the cook. The residual lignin will vary from less than 1% for a well-cooked sulfite pulp to 5% in a raw kraft pulp. Further changes in the pulp on bleaching will be virtually complete removal of lignin, and reduction of the hemicellulose fraction. For a paper pulp this reduction is small. For a dissolving pulp this may amount to removal of all but the most resistant fraction.

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[5] U. S. Bureau of the Census, *Pulp & Paper*, **25**, No. 7, 152 (1951).

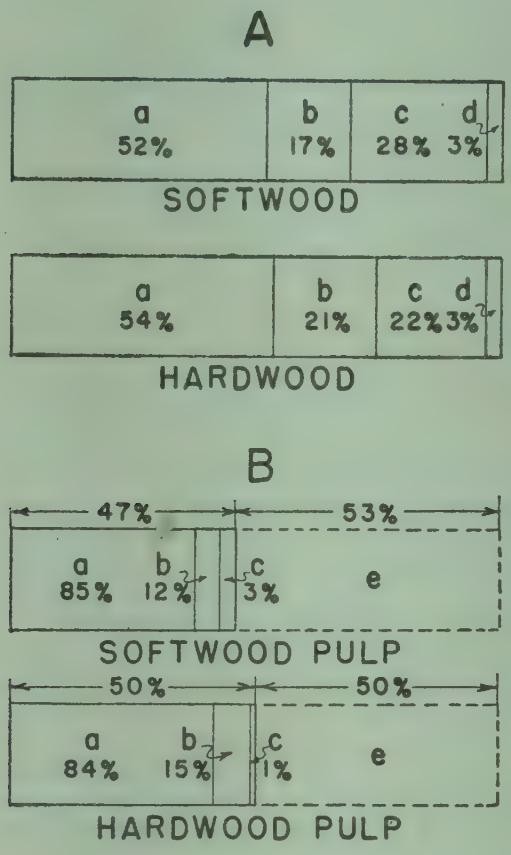

Fig. 1. The approximate chemical composition of softwood and hardwood, and of pulps prepared from them. (A) Wood; (B) pulp; (a) cellulose, (b) hemicelluloses, (c) lignin, (d) extractives, (e) loss in pulping. All percentages in A based on total wood, those in B on pulp.

(b) STRUCTURE OF THE CELL WALL

Some familiarity with the microstructure of wood is necessary to understand the processes of pulping. The arrangement of the fibers in wood and their relation to each other have been discussed in Chapter V-A. The wood technologists' conception[6,7] of the structure of the cell wall is shown in Figure 2.

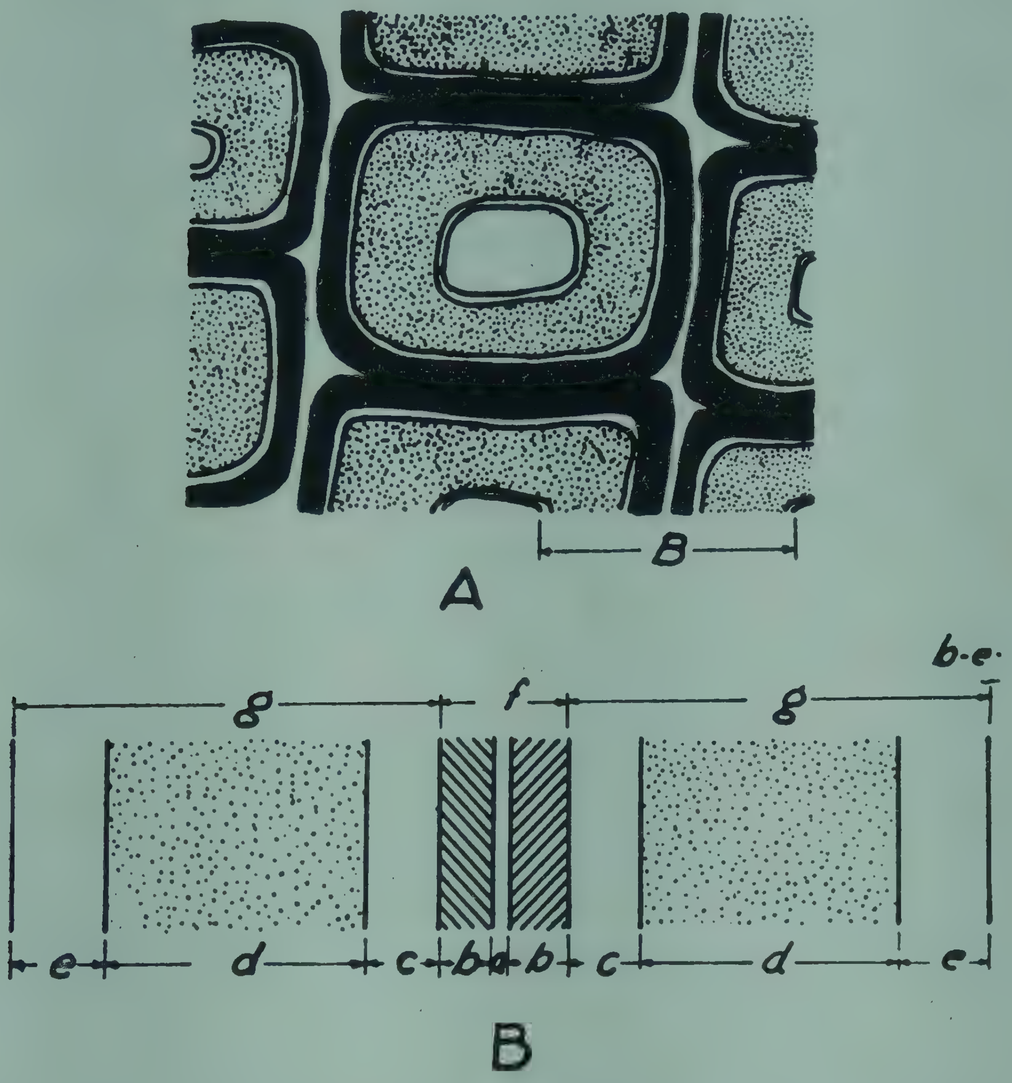

Fig. 2. The compound cell wall of wood fibers (Jahn and Holmberg[7]). Cell wall parts according to I. W. Bailey.

(A) Cross section of fiber
(B) Section of two adjacent cell walls
(*a*) Intercellular substance
(*b*) Primary (cambial) wall
(*c*) Outer layer secondary wall
(*d*) Central layer secondary wall
(*e*) Inner layer secondary wall
(*f*) Compound middle lamella
(*g*) Complete secondary wall
(*b–e*) Complete cell wall of one fiber

For some time it has been thought from observation of stained wood sections that a large portion of the lignin is concentrated in the compound middle lamella (the region represented in Figure 2 by the portion labeled *f*),

---

[6] I. W. Bailey, *Ind. Eng. Chem.*, **30,** 40 (1938).

[7] E. C. Jahn and C. V. Holmberg, *Paper Trade J.*, **109,** 30 (Sept. 28, 1939).

that is, the intercellular membrane plus the primary wall of the fiber on each side. Bailey[8] gave quantitative support to this observation by devising a microtechnique for isolating a small quantity of middle lamella. In this region of Douglas fir he reported the composition as 71% lignin, 4% cellulose, and 14% pentosans. Lange[9] obtained similar results by optical absorption methods which gave a picture of the composition of the entire

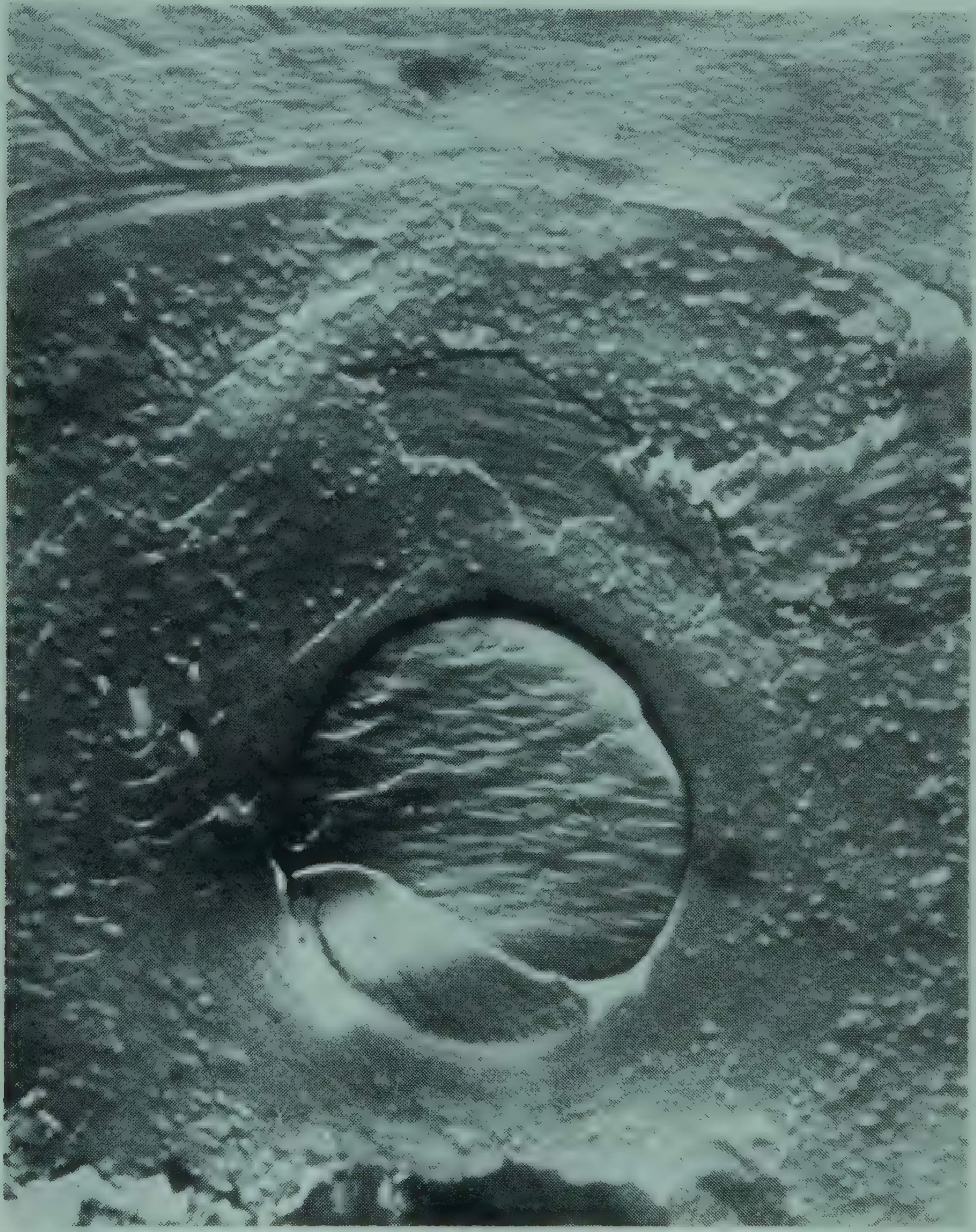

Fig. 3. The surface of an undercooked pine tracheid at a bordered pit showing the lignin sheath and underlying primary fibrillar structure. Note the spot where the lignin sheath is mechanically broken. No description of the membrane under the pit aperture has been advanced (Horio, Kobayashi, and Komagata[10]). Magnification ×7,500.

---

[8] A. J. Bailey, *Paper Ind.*, **18**, 379 (1936); *Ind. Eng. Chem., Anal. Ed.*, **8**, 52, 389 (1936).

[9] P. W. Lange, *Svensk Papperstidn.*, **48**, 241 (1945); *Chem. Abstracts*, **39**, 3661 (1945).

cell wall. He also found 70% lignin in the middle lamella. There was a sharp decrease in lignin content in the secondary wall with further decrease toward the lumen. Hemicellulosic material was found to be more concentrated near the middle lamella than adjacent to the lumen. Horio,[10] using chromium shadow technique, has recently obtained striking optical confirmation in an electron micrograph of the surface of a very raw fiber (Fig. 3). The surface appeared very smooth in the picture, but on one spot the surface layer had been chipped much as an enamel coating might be, and underneath the fibrillar structure of the cellulose fiber was exposed.

(c) DEFINITION OF AND REMARKS ON PULPING

Chemical pulping of wood may be defined as a process in which the fiber-cementing material (lignin) is dissolved by reasonably specific reagents, and the individual fibers are liberated.

In the laboratory the reagents used to isolate holocellulose[11] are quite specific in their removal of lignin. In commercial operation none of today's practical pulping agents can even approximate this quantitative removal of lignin, and one of the major challenges to the industry is a more efficient recovery of cellulose. A more complete removal of lignin in the cook would entail an unreasonable loss of cellulose. On the other hand, increasing yield by cooking less results in a greater proportion of lignin to cellulose. Since the lignin is concentrated on the surface of the fiber, papermaking properties are then impaired.

Lewis and Richardson[12] prepared from a single sample of wood a series of raw alkaline pulps in which the various pulps had a progressively smaller amount of lignin. The beating characteristics and the swelling behavior in cuprammonium hydroxide of these pulps were determined. As the lignin content of the pulps decreased from 22.2 to 8.6%, the pulps beat more readily, felted more satisfactorily into handsheets, and attained higher physical tests. Cuprammonium hydroxide had almost no effect on the pulp with 22.2% lignin. As the lignin content of the pulps decreased, a "ballooning" type of swelling began to occur on contact of the fibers and reagent. It appeared that swelling was restricted by a resistant sheath surrounding the fiber. Wherever this sheath was absent or weakened, the fiber would swell to several times its diameter giving the appearance of a series of balloons. This study supported the hypothesis that wood fibers, as they naturally occur, are surrounded by a sheath of high lignin content. (See also Chapter IV-C for a discussion of swelling and ballooning of cellulose fibers.)

---

[10] M. Horio, K. Kobayashi, and O. Komagata, unpublished work.

[11] W. G. VanBeckum and G. J. Ritter, *Paper Trade J.*, **105**, 127 (Oct. 28, 1937).

[12] H. F. Lewis and C. A. Richardson, II, *Paper Trade J.*, **109**, 48 (Oct. 5, 1939).

Commercial pulping of wood, then, is always a compromise. Although lignin is largely concentrated in the middle lamella, its distribution throughout the secondary wall makes it difficult to remove quantitatively. On the other hand, the lower carbohydrates are rather easily soluble in pulping chemicals, and under conditions necessary to meet commercial pulping schedules, even the resistant cellulose is attacked. The common pulping reagents in use today in order of decreasing specificity in rendering lignin soluble are:

Most specific: Chlorine
Sodium sulfite plus sodium bicarbonate
Sulfurous acid plus a bisulfite
Sodium hydroxide plus sodium sulfide
Least specific: Sodium hydroxide

Although it is the best of the commercial pulping agents, chlorine cannot be used on wood because of its cost. Its use is confined to pulping grasses in which the lignin content is low, or to bleaching wood pulp after the bulk of the lignin has been removed. The mild action of sodium sulfite in the mildly alkaline range is too slow for general pulping, and its use is generally limited to production of high-yield pulps. The specific action of the sulfite ion in sulfurous acid plus a bisulfite is partially nullified by the hydrolytic action of the acid. The net result is that acid sulfite is less specific than neutral sulfite. In general, strong alkali is the least specific of the commercial pulping agents because of its rather slow action on lignin and its tendency to attack carbohydrates. Sodium sulfide greatly increases the rate of dissolution of lignin, and thus improves specificity. Although sodium hydroxide was the first successful chemical pulping agent, its use is now limited to cooking hardwood.

One of the most significant points evident from the above list is the importance of sulfur in commercial pulping. Virtually all of the wood pulp is cooked with some form of sulfur—alkaline sulfide in kraft, acid sulfite in the sulfite process, and mildly alkaline sulfite in the neutral sulfite process. The reactivity of these forms of sulfur with lignin, and the cheapness of these chemicals indicate that sulfur will remain of prime importance in pulping for at least the foreseeable future.

(d) STEPS IN CHEMICAL PULPING COMMON TO ALL PROCESSES

For a better understanding of the ensuing discussion it is desirable at this time to describe the steps in wood pulping in a very general way. More specific remarks will be made on each process in separate sections.

(1) *Wood Preparation*

Bark must be removed from the wood since in the cook it would be a source of dark color and dark fibers in pulp. Barking is sometimes done by hand-peeling the logs in the woods while the bark is loose in the early rush of growth in spring. More commonly it is done mechanically at the mill. The logs are reduced to 4-foot or sometimes 8-foot lengths, and fed into one end of a large, horizontal drum which is constructed from steel bars. The drum is rotated on its longitudinal axis and the bark is knocked off by the bolts of wood falling against each other and the steel drum. Bark drops from the drum between the bars, and the wood being fed in one end of the drum forces the flow from the other end. The most recent method of barking is to direct a high-pressure jet of water perpendicularly to the axis of the log, and either by turning the log and moving the jet along its length, or by rotating the jet and moving the log past it, the bark is removed. In some installations the log is passed through a ring of water jets which remove the bark. Water pressures up to 1400 lb./sq. in. are used.

The wood must be reduced to units small enough so that the cooking liquor can penetrate completely and uniformly in a reasonable time. This is done by cutting chips which have the preferred dimensions: $^5/_8$ to $^7/_8$ inch in length, $^1/_{16}$ to $^1/_8$ inch in thickness, and $^1/_2$ to 1 inch in width.

(2) *Digestion*

Chips are fed into large steel pressure vessels known as digesters, which have capacities ranging from 1500 to 3500 cu. ft. for kraft, and from 3500 to 12,000 cu. ft. for sulfite. Cooking liquor is added, and the contents of the digester are heated with steam and under pressures ranging from 75 to 125 lb./sq. in. according to a predetermined cooking curve. When the wood has been cooked, the softened chips and spent liquor are discharged from the digester by blowing under pressure into pits or tanks.

(3) *Washing and Screening*

The pulp is freed from spent liquor by washing, and is screened to remove uncooked wood. A coarse screen or knotter first removes uncooked chips and knots from the dilute water suspension of pulp, and then fine screens remove the uncooked fiber bundles. The pulp can then be used in the unbleached state, or further purified by bleaching.

2. Physical and Chemical Factors in Pulping

(a) PENETRATION OF WOOD BY LIQUIDS

One of the first considerations in pulping is the need to bring the cooking liquor into intimate contact with all portions of the chip so that delignification can proceed uniformly. The most extensive studies in this field were made by Maass and coworkers whose work has been summarized by Beazley, Johnston, and Maass.[13] The principal path of penetration in the chip is longitudinal, that is, parallel to the fiber length. As a rough average, penetration in this direction is 100 times as rapid as in either radial or tangential direction. The one exception to this is sodium hydroxide solution or an equivalent strong alkali, which can penetrate wood with almost equal rapidity from any direction. The flow through sapwood is much greater than through heartwood of the same species. Rate of flow increases with temperature faster than can be explained on the basis of viscosity–temperature relations. Air in the fiber lumens greatly hinders penetration. Contrary to popular belief, resins have only a minor retarding effect. Penetration of jack pine increased only 20% on removal of resins. McGovern and Chidester[14] have demonstrated that wetting agents as a class do not facilitate penetration of wood by cooking liquor. Wetting agents promote surface wetting through lowered surface tension of the liquid, but since capillary rise is important in penetration, and since it decreases with decrease in surface tension, wetting agents actually decrease penetration. Poorer penetration was observed in cooks to which wetting agents were added.

(b) EFFECT OF TEMPERATURE

Temperature increases the rate of digestion of wood. Maass and coworkers[15] found that the rate of delignification approximately doubles for a rise in temperature of 10°C. In commercial practice, high temperatures are frequently used to increase the rate of cooking. However, this practice is not without its drawbacks, since cellulose suffers degradation from heat, and this effect also increases with temperature. McGovern and Chidester[16] found that in the range of 130–150°C. pulp yields suffered a loss of 0.5% for an increase of 10°C., and physical properties of the pulps were degraded.

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[13] W. B. Beazley, H. W. Johnston, and O. Maass, *The Penetration into Wood of Cooking Liquors and Other Media*, Canada Dept. of Mines and Resources, Lands, Parks, and Forests Branch, *Dominion Forest Service, Bull.* No. **95**, Ottawa, 1939.

[14] J. N. McGovern and G. H. Chidester, *Paper Trade J.*, **111**, 35 (Dec. 12, 1940).

[15] A. J. Corey and O. Maass, *Can. J. Research*, **14B**, 336 (1936); J. M. Calhoun, F. H. Yorston, and O. Maass, *Can. J. Research*, **17B**, 121 (1939).

(c) EFFECT OF CHEMICAL CONCENTRATION

An increase in the concentration of cooking chemical will increase the rate of delignification.[17–20] Since in sulfite pulping one of the chemicals, sulfur dioxide, is a gas, an increase in the concentration of the cooking liquor must be accompanied by an increase in digester pressure in order to maintain the concentration. In general, it has been found that both yield and physical properties of pulp are less sensitive to an increase in chemical concentration than to an increase in temperature. Within reasonable limits it is preferable to increase the rate of cooking with chemical concentration.

(d) EFFECT OF WOOD PROPERTIES

The cellulose in a fiber can be said to have its optimum properties while it is still a unit in sound wood. Any pulping reaction subtracts from this optimum condition. It seems obvious then that the properties of wood have a basic relation to the properties of pulp.

(1) Sapwood and Heartwood

Sapwood is the ring of light-colored wood adjacent to the bark. Although no longer alive and growing, this wood is still taking part in the life process by transporting water from the roots to the crown of the tree. Heartwood is the darker wood in the center of the trunk. This wood no longer takes part in the life process and contributes only strength to the trunk. Its darker color is caused by the deposition of coloring matters, resins, etc. McGovern and Chidester[21] reported that there was relatively little difference in pulps from pulping of sapwood and heartwood. The drier condition and extractives in heartwood made pulping slightly more difficult. Pulps from sapwood tended to have a lower burst and higher tear. In some species where the extractives have a specific effect on the pulping reaction, there is marked difference in pulping of heartwood and sapwood. This will be discussed later.

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[16] J. N. McGovern and G. H. Chidester, *Paper Trade J.*, **106**, 39 (June 2, 1938).

[17] J. N. McGovern, *Paper Trade J.*, **103**, 29 (Nov. 12, 1936).

[18] M. W. Bray, J. S. Martin, and S. L. Schwarz, *Paper Trade J.*, **105**, 39 (Dec. 9, 1937).

[19] W. F. Holzer, *Paper Trade J.*, **118**, 35 (Apr. 20, 1944).

[20] W. Pittam, *Tech. Assoc. Papers*, **29**, 613 (1946); *Pulp & Paper*, **21**, 76 (Nov., 1947).

[21] J. N. McGovern and G. H. Chidester, *Paper Trade J.*, **107**, 34 (Oct. 6, 1938).

(2) *Springwood and Summerwood*

The alternate light and dark rings visible in the cross section of a log mark the annual growth of the tree. Each year one light-colored ring and one dark-colored ring are formed. The first, springwood, consists of large-diameter, thin-walled fibers which are formed when there is need for a large volume of water for growth in spring. The second, summerwood, has smaller diameter, thick-walled fibers formed during summer. Probably because of the large difference in the wall thicknesses, the relative amounts of springwood and summerwood have a marked effect on pulp properties. Holzer and Lewis[22] separated springwood and summerwood of Douglas fir by hand methods and cooked them separately. Springwood cooked with more difficulty, gave lower yields, had a higher burst but lower tear than summerwood. After beating, the springwood fibers were badly cut and fibrillated; the summerwood fibers showed little visible effect. Hammond and Billington[23] found that burst, fold, and sheet density increased with the percentage of springwood while tear decreased. McGovern and Chidester[24] reported an increase in springwood from butt to top of the tree. There was a decrease in yield, a small decrease in burst, and a large decrease in tear in pulps in the same direction. These same investigators[25] in a study of the southern pines found a greater difference from a 10% increase in percentage of springwood, than among the various species studied.

The ratio of springwood to summerwood appears to be one of the most critical physical characteristics of wood in determining pulp properties. Since the ratio will change with rate of growth, with the age of the tree, and from bottom to top, it is readily realized that very little control can be exercised by the pulp producer. This is one excellent example of the heterogeneity of wood, and serves to emphasize that any pulp property can only be an average of the properties of the individual fibers.

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[22] W. F. Holzer and H. F. Lewis, *Tappi*, **33,** 110 (1950).

[23] R. N. Hammond and P. S. Billington, *Tappi*, **32,** 563 (1949).

[24] J. N. McGovern and G. H. Chidester, *Paper Trade J.*, **106,** 37 (June 9, 1938).

[25] G. H. Chidester, J. N. McGovern, and G. C. McNaughton, *Paper Trade J.*, **107,** 36 (July 28, 1938).

(3) *Species*

The principal effect of species is that of fiber properties as determined by growth habit. The largest difference due to species is between hardwoods and softwoods. The former have fibers to the order of 1 mm. long and 10–25 microns in diameter. The latter have fibers from 2.5 to 4.5 mm. long with diameters of 25–50 microns. Aside from this there are characteristic differences in various softwood species. For example, fibers in species characteristic of eastern Canada and northern United States from the Great Lakes eastward, are shorter and narrower than those found on the Pacific Coast or in the South. Papers made from the finer fibers tend to be better formed and smoother; those from the coarser fibers will have poorer formation, rougher surface, but better tearing strength. Space will not permit specific comment possible on nearly every species.

Other variations within the species include pigments which affect color and bleachability of the pulps; extractives which well may cause trouble in cooking from pitch deposits in the system, or reduced pulp yields; density which will affect pulp yield and production; lignin content which can alter the ease of cooking; and hemicellulose content which has direct relation to physical pulp properties.

(4) *Decay in Wood*

When wood was plentiful and demand was small, only the best and soundest was used. Now that supplies are limited and demand is sharply up, all the wood must be used, and each forest industry must use down through the lowest quality it can tolerate. Since lower quality wood can be used for pulping than for lumber, much decayed wood finds it way to the pulp mill. Holzer[26] described the effect of wood decay on pulp properties. Pulp becomes noticeably darker with incipient decay, and suffers further loss in brightness as decay progresses. The acid formed in the process of decay renders lignin less soluble and noticeably slows the rate of cooking. Fiber properties begin to deteriorate as decay reaches an intermediate stage. Wood substance is lost in such proportions in advanced decay that pulp yield and production suffer. In practice the use of decayed wood must be so programmed that only small percentages are encountered at any time and that the full effects as described are not felt.

(e) UNIFORMITY

The question of uniformity has been purposely left to the last. Production of a uniform pulp requires a uniform raw material, uniform conditions within each chip, uniform conditions within a digester, and uniform conditions from digester to digester. With the variables in the process, some of which have been indicated, and the variable properties of wood, it is easily imagined that the skill and ingenuity of the operator is constantly being taxed. Although to a certain extent pulp manufacture is an art of balancing these many variables, and will remain so, our more detailed knowledge, better control through instruments, and better equipment are more and more averaging or controlling these variables and reducing the art to a scientific practice.

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[26] W. F. Holzer, *Proc. Forest Products Research Soc.*, **4**, 134 (1950).

3. The Sulfite Process

(a) DESCRIPTION OF PROCESS

It is now desirable to supplement the earlier very general description of pulping by giving certain specific details of the sulfite process. A more complete description may be found in the literature.[27,28]

(*1*) *The Cooking Acid*

Sulfite cooking acid is a solution of sulfur dioxide and a bisulfite. The latter may be an alkali or alkaline earth, but usually for economic reasons it is calcium or dolomite. In recent years magnesium, sodium, or ammonium bisulfite are being used in commercial processes. The industry expresses the chemical concentration in terms of "total," "free," and "combined" sulfur dioxide according to the following definitions:

Total: The total concentration of sulfur dioxide whether present as sulfurous acid, bisulfite, or dissolved sulfur dioxide.

Free: The amount of sulfur dioxide in excess of the theoretical amount to form monosulfite.

Combined: The amount of sulfur dioxide required theoretically to form monosulfite.

In each case the concentration is reported as "per cent" SO_2, but the figure as determined is actually grams per 100 ml. The total and free are most commonly determined by the method of Palmrose.[29] Combined is determined by difference.

Acid is prepared by burning sulfur to form sulfur dioxide, cooling the gas

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[27] G. H. McGregor, in J. N. Stephenson, editor, *Pulp and Paper Manufacture*, Vol. 1, McGraw-Hill, New York, 1950, Chapter 4; J. P. Casey, *Pulp and Paper*, Vol. I, Interscience, New York-London, 1952, pp. 74–132.

[28] *Chemipulp Sulfite Mill Operation*, Chemipulp Process, Inc., Watertown, N. Y., 1939, 191 pp.

[29] G. V. Palmrose, *Paper Trade J.*, **100**, 38 (Jan. 17, 1935).

rapidly, and absorbing the sulfur dioxide in water in the presence of the base. Usually the base is limerock, and conditions are controlled to dissolve just the required amount. The sulfur dioxide concentration is raised to the desired level by the absorption of return or "relief" gas from the digesters. About five times as much sulfur dioxide as is actually used is put into the digester. The excess, being a gas, tends to escape, and is returned to the acid through a relief system. A typical cooking acid contains 6.5% total SO_2, 5.3% free, and 1.2% combined.

(2) *The Cooking Cycle*

The sulfite cooking cycle is divided into three main parts: the penetration period, the cooking period, and the recovery period. Time must be allowed for the chemical, both free and combined, to penetrate the chip completely. The combined, being the slower, is the determining factor. Temperature in the digester is raised slowly over a period of about 4 hrs. to 110°C., at which level the rate of cooking becomes significant. Penetration becomes rapid from about 80°C. on. Following the penetration period the temperature is raised to a maximum, usually between 135° and 145°C. The pressure is allowed to rise until it reaches about 80 lb., after which it is maintained constant by relieving gas. When the cook reaches the proper stage at about the end of the seventh hour from the start, pressure is reduced to 30 lb. during a period of about 1.5 hrs. in order to recover chemical. The cook finishes during the recovery period, and at the end is blown into a pit by the remaining digester pressure. The total cooking time is about 8.5 hrs.

(3) *The Pulp*

Sulfite pulp as discharged from the digester has a grayish-white color. Yields of pulp on the basis of dry wood are 46–48%. The pulp is of medium strength and very versatile in its papermaking qualities. It is mixed with groundwood to make newsprint; it will make soft papers such as napkins and the various sanitary tissues; and it will produce excellent bond papers. Further, by adjustment of the cooking, and with further chemical purification, it is the raw material for cellulose derivatives, as a replacement for or supplement to cotton linters.

(b) PROGRESS OF THE COOKING PROCESS WITH TIME

The removal of lignin from the cell wall during the sulfite cook has been followed photographically. Bixler[30] pulped wood sections and studied the removal of lignin with staining techniques. The intercellular material was removed first, but attack was started on the secondary wall before the removal of the intercellular material was complete. The primary or cambial wall persisted through the entire cook. Lange[9, 31] made similar studies using ultraviolet absorption methods. The lignin in the middle lamella was attacked in the early stages of the cook. However, the ultraviolet

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[30] A. L. M. Bixler, *Paper Trade J.*, **107**, 29 (Oct. 13, 1938).

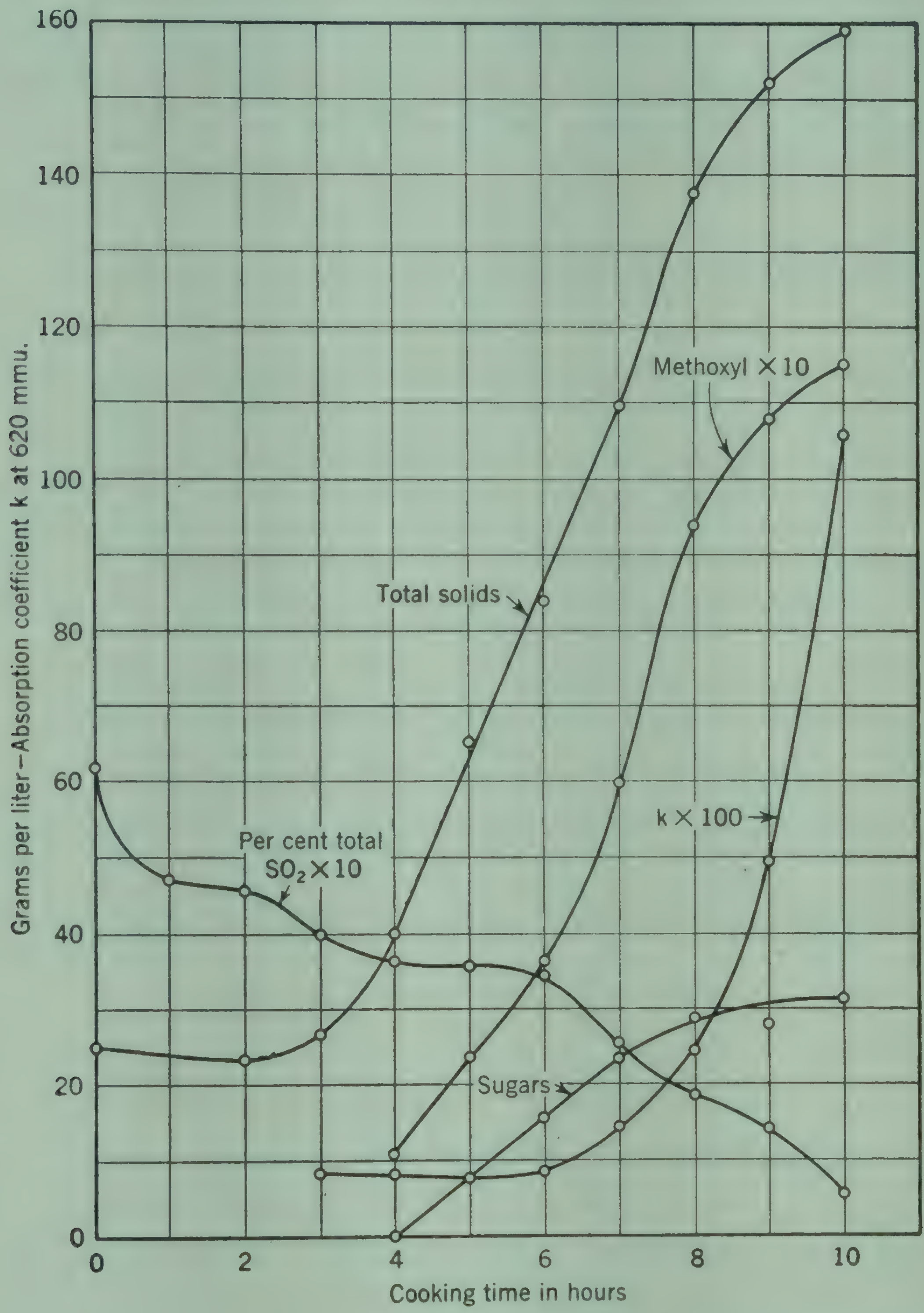

Fig. 4. The concentration of chemical components and coloring matter as a function of reaction time in sulfite pulping (Simerl[32]).

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[31] P. W. Lange, *Svensk Papperstidn.*, **50**, 130 (1947); through *Chem. Abstracts*, **41**, 7112 (1947).

[32] L. E. Simerl, *Tech. Assoc. Papers*, **23**, 114 (1940).

absorption spectrum did not change, indicating that no deep-seated reaction with the benzene nucleus of the lignin took place. Lange observed dichroism in the intercellular material which indicated a degree of orientation in the lignin. The dichroism weakened during the cook and had disappeared by the time the fibers were separating. This was interpreted as strongly suggesting that the lignin was not only the cementing material between the fiber, but that there was some sort of bond between the lignin and cellulose. It was also suggested that the path of penetration of the cooking liquor was through the middle lamella, and was not by diffusion through the cell wall from the lumen.

The appearance of dissolved materials in the digester liquor during cooks of several species of wood was determined by Simerl.[32] Figure 4 presents typical curves for the total sulfur dioxide, total solids, methoxyl, sugars, and light absorption coefficient as a function of reaction time of a cook on black spruce (*Picea mariana*) made under the following conditions:

Sulfur dioxide concentration:	
Total	6.2%
Free	5.0%
Combined	1.2%
Liquor: oven-dry wood ratio	3.6 ml./g.
Time to 110°C.	3.0 hrs.
Time 110–140°C.	4.0 hrs.
Time at 140°C.	3.0 hrs.
Maximum pressure	75 lb./sq. in.

Linear relief to blowing pressure of 50 lb./sq. in. during last hour.

The color development of the liquor during the cook could be divided into three stages. During the first 3 hrs. the color was light yellow due to extraction of water solubles and to small amounts of lignosulfonic acid. About the third hour it changed gradually to a reddish brown with appearance of larger quantities of lignosulfonic acid. This color deepened and during the last 2 hrs. turned to a coffee brown due to decomposition of carbohydrates. These changes can be traced in the curves. Starting with the third hour the methoxyl content, an indication of the lignin present in the liquor, and the total solids increased in parallel fashion. Sugars started from zero at the fourth hour and increased to 30 g. per liter at the eighth hour, after which there was little further change. The absorption coefficient at 620 millimicrons, an indication of the depth of color of the liquor, did not change until the sixth hour and then developed at a progressively accelerated rate. Because the absorption coefficient curve was not parallel to any of the curves of the chemical constituents, Simerl suggested that the rapid color change during the last 2 hrs. was due to degradation of carbohydrates. This is corroborated in commercial practice by the appearance of carbon dioxide in relief gases toward the end of the cook.

(c) THEORY OF THE SULFITE PROCESS

Modern theories of the reaction in the sulfite cook had their inception when Pedersen[33] and Lindsey and Tollens[34] first showed that pulping was due to the reaction of lignin and sulfite to form a soluble lignosulfonic acid. The development of the subject has been controversial and a detailed discussion would be only of historical value. The most widely accepted theory today is the one evolved by Hägglund[35] from work extending over the past thirty years. The removal of lignin from wood takes place in two steps, first the sulfonation of lignin in the solid state, and second the dissolution of this solid lignosulfonic acid.

The formation of the primary solid lignosulfonic acid can be demonstrated by cooking wood with a sodium bisulfite solution at a pH of 6. Sulfonation takes place rapidly until one sulfur atom has been added for every three to four methoxyl groups. At this level sulfonation almost ceases, and practically no lignin dissolves. If the pH is lowered to 4.5 the degree of sulfonation reaches one sulfur atom per two methoxyl groups, but still solution of lignin is very low. Lignosulfonic acid can be dissolved from the sulfonated wood by heating in an acid buffer solution. The rate of dissolution increases with lower pH. Then, too, if sulfonated wood is treated with a strong mineral acid, the base associated with the lignosulfonic acid is removed leaving the solid free acid. This acid, known as Kullgren acid, can be dissolved merely by heating the wood in water. Hydrogen ions are furnished by the lignosulfonic acid itself.

The hydrogen-ion catalysis of the dissolution of solid lignosulfonic acid appears to be a hydrolytic action. It can be assumed that the lignin is joined to some carbohydrate material or polymerized into large insoluble lignin molecules through acetal-like bonds. The hydrolytic splitting of these bonds by hydrogen ions breaks the lignosulfonic acid into simpler units which are soluble.

At the International Congress of Pure and Applied Chemistry held in New York in September 1951, the consensus was that these acetal bonds were between low lignin polymers and not between lignin and a carbohydrate.

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[33] N. Pedersen, *Papier-Ztg.*, **15**, 422, 787 (1890); E. Hägglund, *Chemistry of Wood*, 3d ed., Academic Press, New York, 1951, p. 415.

[34] J. B. Lindsey and B. Tollens, *Ann.*, **267**, 341 (1892); E. Hägglund, *Chemistry of Wood*, 3d ed., p. 415.

[35] E. Hägglund, *Chemistry of Wood*, 3d ed., pp. 215, 415; *Tappi*, **33**, 520 (1950).

Erdtman[36] and his coworkers[37] describe the reaction with model substances which can be simplified as follows:

A—Lignin—B

"A" is a group which will sulfonate readily in neutral or mildly acid solution. It occurs in the lignin molecule, probably as a benzyl hydroxyl group. "B" will sulfonate only in strongly acid solution. This is probably an acetal group linking lignin into larger molecules, either to carbohydrate material or into a larger polymer of lignin.

Calhoun, Yorston, and Maass[38] claim that the second step in the solution of lignosulfonic acid as described by Hägglund is controlled not alone by pH, but by a combination of pH and concentration of bisulfite ions. They prepared three solid lignosulfonic acids in wood with sulfur contents, on the basis of the lignin, of 4.2, 5.1, and 6.2%. The first sample in a buffer at pH 2 delignified only slightly, the second to a level of 1.5% lignin, and the third to 0.3% lignin. The first sample cooked more slowly than in sulfite liquor, the second about the same as in sulfite liquor, and the last much more rapidly. When a portion of the third sample was cooked in a buffer at pH 3, it cooked about as it did in sulfite liquor. However, this third sample in sulfite liquor at a constant pH cooked more rapidly as the concentration of the base was increased. It was concluded that the dissolution of the solid lignosulfonic acid was controlled both by the hydrogen and bisulfite ions present.

Brauns and Brown[39] methylated sprucewood meal with diazomethane. This wood, methylated under very mild conditions, could not be cooked with sulfite acid. The lignin became partially sulfonated, but could not be solubilized. Apparently the first stage of the sulfonation as postulated by Hägglund took place at least to some extent, but the second stage of the reaction was blocked by the methoxyl group.

(d) EFFECT OF PRETREATMENTS ON THE SULFONATION OF LIGNIN

Several investigators have studied the effects of pretreatments on the sulfite reaction. Corey and Maass[40] have heated wood in water and in various buffers for varying lengths of time and at different temperatures. Such treatments retard subsequent delignification. The effect is greater at higher temperatures and longer times. With regard to pH the inhibiting action is least at pH 4.6. Richter[41] carried on a series of two- and three-stage cooks. If the first stage subjected the wood to high temperatures, the lignin became almost inert to later sulfonation. However, if the wood were first sulfonated, treatments which, when carried on initially, rendered lignin insoluble, now had no effect. It seems reasonable to suggest that lignin under the influence of heat or acid in the presence of moisture polymerizes to an insoluble form. If the lignin is first sulfonated, the group through which polymerization takes place is blocked, and the balance of the sulfonation and dissolution can proceed without change.

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[36] H. Erdtman, *Tappi*, **32**, 75 (1949).

[37] B. O. Lindgren and U. Saedén, *Svensk Papperstidn.*, **54**, 795 (1951).

[38] J. M. Calhoun, F. H. Yorston, and O. Maass, *Can. J. Research*, **15B**, 457 (1937).

[39] F. E. Brauns and D. S. Brown, *Ind. Eng. Chem.*, **30**, 779 (1938).

[40] A. J. Corey and O. Maass, *Can. J. Research*, **13B**, 149 (1935); **13B**, 289 (1935).

A practical example of the above is that of "red-centered" chips in cooking. The sulfur dioxide of the cooking acid penetrates the chip faster than the calcium base. If the temperature gets too high before the base reaches the center of the chip, the sulfonation reaction starts, but the lignosulfonic acid is not neutralized. The acidity and heat renders the unsulfonated lignin insoluble, and the chip remains uncooked. In a "burnt" cook the base is exhausted before the cook is completed, the liquor becomes extremely acid, and the lignin is reprecipitated on the fiber. The dark pulp from such a cook is almost impossible to bleach. It is interesting to note that when ammonia is substituted for calcium as the base, it is almost impossible to raise the temperature fast enough to obtain red-centered chips. This indicates that the ammonium ion penetrates the chip with approximately the same speed as the bisulfite, and much faster than calcium.

(e) KINETICS OF THE SULFONATION OF LIGNIN

Several studies have been made on the kinetics of the sulfite reaction at the Pulp and Paper Research Institute of Canada.[42] This work demonstrated that the sulfonation of lignin approximates a first-order reaction, that is, the rate at which lignin was dissolved from wood was approximately proportional to the lignin remaining. Deviation was most pronounced at the beginning of the cook when the rate of solution was slower than would be predicted. Goldfinger,[43] using these data,[42] made a theoretical study of the reaction and found that the energy of activation of lignin solution started at 16,000 calories per mole and increased to 22,500 calories per mole at the end of the cook. Equations, describing the reaction as a surface adsorption, followed by an activated adsorption, and finally the true reaction, fitted the data[42] reasonably well.

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[41] G. A. Richter, *Tappi*, **32**, 553 (1949).

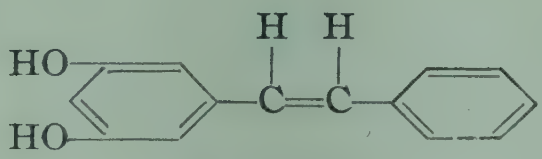
[42] F. H. Yorston, *Proc. Tech. Sect., Can. Pulp and Paper Assoc.*, **1935**, 91; A. J. Corey and O. Maass, *Can. J. Research*, **14B**, 336 (1936); J. M. Calhoun, F. H. Yorston, and O. Maass, *Can. J. Research*, **15B**, 457 (1937).

[43] G. Goldfinger, *Paper Trade J.*, **112**, 29 (June 12, 1941); **113**, 27 (Oct. 9, 1941).

Bryde[44] studied the kinetics of the sulfite reaction by making short cooks in which ammonia was gassed into an evacuated bomb filled with chips, sulfur dioxide solution was added, and the temperature was raised rapidly. He found three characteristic subdivisions in the series, namely: the region where lignin removal was in the range of 0–7%, where it was 7–25%, and where it was 25–28%. The sulfur in the lignin increased rapidly until it reached a ratio of 1 S:4 $C_9H_9OCH_3$ (first stage); the sulfur content then increased more slowly until it reached a ratio of 1 S:2 $C_9H_9OCH_3$ (second stage); a further increase to liquor blackening was followed by a decrease (third stage). These stages were related to: first, the breaking-down of the middle lamella and splitting of the presumed bond between lignin and carbohydrates; second, the dissolution of lignin; and third, the attack on the carbohydrates.

(f) LIMITATIONS OF THE SULFITE PROCESS

Certain species of wood can be pulped by the sulfite process only with difficulty or under special conditions. The most common of these are the pines and Douglas fir. It was first believed that the resins in the wood hindered penetration. Following preliminary work by Hägglund and Schwalbe, Erdtman[45] isolated and identified a phenol from pine heartwood which he showed to have the power of inhibiting the sulfite cook. This compound, which he named pinosylvin, is a stilbene derivative:



Pinosylvin

The monomethyl ether was also isolated. Further studies showed that many phenols including pyrogallol, resorcinol, phloroglucinol, catechin, naphthols, and the like will strongly inhibit the sulfite cook. Pinewood was cooked successfully by sulfonating first in slightly alkaline sodium sulfite, and then cooking normally.

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[44] Ø. Bryde, *Finnish Paper Timber J.*, **29**, 296 (1947); through *Chem. Abstracts*, **42**, 5220 (1948).

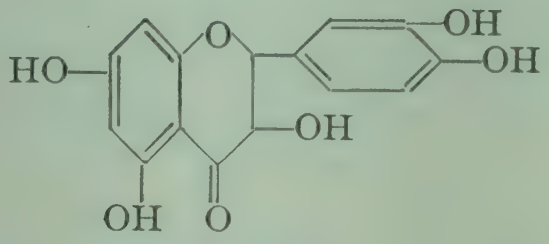
[45] H. Erdtman, *Ann.*, **539**, 116 (1939); through *Chem. Abstracts*, **33**, 7098 (1939); *Tappi*, **32**, 303 (1949).

This behavior is explained on the basis of the presence of two kinds of groups in lignin:

(*1*) Those which will react with sulfite easily, but with phenols only under very acid conditions. These are the groups which sulfonate in the first stage of the process.

(*2*) Those which will react with sulfite under acid conditions, but not with phenols. These groups are the ones involved in the hydrolytic stage of the reaction.

If the first groups are blocked by sulfite before the phenols have the opportunity of reaction, the process proceeds normally. Douglas fir (*Pseudotsuga taxifolia*) also has a compound in its heartwood which inhibits the sulfite cook. Pew[46] has isolated the compound and identified it:



Taxifolin

This flavanone has been given the name taxifolin. According to chemical structure it is dihydroquercetin. Its behavior is apparently the same as pinosylvin in pines.

(g) ACID-SUSCEPTIBLE WOOD

In a study of some unexpected variations of pulp strength found in different wood samples, Green and Yorston[47] found that certain areas in wood became brittle on treatment with SO_2 or other dilute acids, while the balance of the wood retained its soft fibrous character. The wood which became brittle they termed "acid susceptible." When isolated and cooked, such wood produced a pulp with inferior strength and a shorter fiber length. It is usually found around compression wood (wood subjected to compressive strains in growth such as on the outside of the curve of a tree which has righted itself in growth after being bent), or around compressive injuries. They extended their studies to chips and found that the second cut, in which the bevel of the knife crushed the wood, caused acid susceptibility. The strength loss from acid-susceptible wood was much lower from an alkaline cook. Grondal[48] also reported damage to cell walls and to

[46] J. C. Pew, *Tappi*, **32**, 39 (1949).

[47] H. Green and F. H. Yorston, *Pulp & Paper Mag. Can.*, **40**, 244 (1939); **41**, 123 (1940).

[48] B. L. Grondal, *Pacific Pulp Paper Ind.*, **13**, 12 (July, 1939).

pulp strength from compressive injuries. He observed microscopic longitudinal cracks in the walls. An observation by Hägglund[49] may be a partial explanation. He found that the pH of a cooking liquor increased from 2.3 to 3–4 as it diffused into the cell wall, and stated that this decrease in acidity protected the cellulose from serious degradation. The cracks observed by Grondal would allow penetration of the acid without decrease of pH. As further evidence, chips made by sawing to avoid compressive damage yielded a sulfite pulp with a burst equal to kraft.[50] It seems probable that the difference in burst between normal sulfite and kraft pulps is caused primarily by this abnormal penetration and concomitant hydrolytic degradation.

(h) VARIOUS BASES USED IN SULFITE COOKING

Several bases in the alkali and alkaline earth groups are being used commercially. Calcium or the natural calcium–magnesium mixture, dolomite, is the commonest because of low cost. Hatch[51] has described the use of magnesium, stating that there is very little difference between magnesium-base and calcium-base pulps. Similar conclusions were reached by Schur and Baker[52] when comparing sodium base to calcium base. Chidester and Billington[53] took advantage of the solubility of sodium salts and studied the effect of varying combined SO_2 from 0.9 to 6.0%. They found that yields and strength values went through a maximum between 2 and 3% combined and dropped to a minimum at 5%. LaFond and Holzer[54] reported on a commercial trial with ammonia base in which it was found that pulp strength and yield improved while cooking time decreased, as compared to a dolomite base. A patent[55] covering a controlled pH, sodium-base pulping has been issued recently. According to this patent, pulps of the sulfite type can be prepared with any desired alpha-cellulose content up to 98% in one pressure cycle. A system for recovery of both sodium ion and sulfur has been developed.

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[49] E. Hägglund, *Svensk Papperstidn.*, **39**, 95 (1936); through *Chem. Abstracts*, **30**, 6560 (1936).

[50] W. F. Holzer, unpublished data.

[51] R. S. Hatch, *Pulp & Paper Mag. Can.*, **47**, 80 (Aug., 1946); *Tech. Assoc. Papers*, **29**, 485 (1946).

[52] M. O. Schur and R. E. Baker, *Paper Trade J.*, **112**, 38 (May 15, 1941); **115**, 33 (Sept. 17, 1942); M. O. Schur and E. G. Ingalls, *Paper Trade J.*, **117**, 34 (Sept. 16, 1943).

[53] G. H. Chidester and P. S. Billington, *Paper Trade J.*, **104**, 39 (Feb. 11, 1942).

[54] L. A. LaFond and W. F. Holzer, *Tappi*, **34**, 241 (1951).

[55] G. Sivola, Canadian Patent 480,404 (Jan. 22, 1952).

The interest in bases other than calcium in the last few years, and, in particular the soluble bases, has been caused by the need for stream improvement through disposal of the spent liquor in ways other than by dumping. The most practical method for general application is to evaporate and burn the liquor. Any heat and chemical recovery will help defray the cost of the operation. The insolubility of calcium monosulfite makes scaling of evaporators a major problem in evaporating calcium-base liquor. It has been done in Sweden in special evaporators in which the flow of steam and liquor can be reversed periodically so that the acid condensate can remove the lime scale.[56] There is no recovery of chemical possible, and the disposal of the calcium ash is a problem. One mill in Sweden is cooking with sodium-base sulfite with recovery of heat and chemicals in a complicated process, the details of which have not been published. Magnesium lends itself to a unique cyclic process[57] since the magnesium salts break down to MgO and SO_2 and both chemicals can be recovered along with large quantities of heat. This process is now in use at the Longview plant of the Weyerhaeuser Timber Company.[58] Ammonia-base sulfite is being used in several mills but no commercial recovery systems have been installed. Pilot plant results[59] have indicated good recovery of heat and SO_2, but the ammonia breaks down to nitrogen and water in the combustion of the liquor.

The manufacture of by-products from spent sulfite liquor has been the subject of extensive research for several decades. The suggested products are numerous. A partial list of commercial products being made today includes ethyl alcohol, vanillin, yeast, tannin extracts, dispersing agents, dye levelling agents, glue extenders, and foundry core binders. In spite of the many types of products possible, there has been no widespread chemical utilization of sulfite spent liquor, primarily because the production cost is not competitive or the volume of product from even one mill would exceed the demand. As yet there are not enough products to utilize all the mill wastes.

4. The Soda Process

Although the soda process was the first historically and although it is still in use, it has never reached the prominence of either sulfite or kraft, and its total production has been static since the beginning of the twentieth century in spite of the enormous expansion of the industry in general. The reason for this has been the superiority of both sulfite and kraft, especially the latter, in yield and strength of pulp, and ease of cooking Production of soda pulp is confined almost entirely to cooking hardwoods In fact, soda pulp in the trade is understood to be made from hardwood unless otherwise specified. The more drastic action of the sodium hydroxide produces a soft, limp fiber which is peculiarly adapted to the furnish of printing papers.

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[56] F. W. Grewin and S. G. Lindberg (to Rosenblad Corp.), U. S. Patent 2,490,750 (Dec. 6, 1949); *Chem. Abstracts*, **44**, 1706 (1950); A. E. Tyden (to Rosenblad Corp.), U. S. Patent 2,490,759 (Dec. 6, 1949); *Chem. Abstracts*, **44**, 2154 (1950).

[57] G. H. Tomlinson and L. S. Wilcoxson, *Paper Trade J.*, **110**, 31 (Apr. 11, 1941).

[58] R. E. Baker and L. S. Wilcoxson, *Tappi*, **33**, 187 (1950).

[59] J. H. Hull and G. V. Palmrose, *Tappi*, **35**, 193 (1952).

(a) DESCRIPTION OF THE PROCESS

(1) *The Cooking Liquor*

Soda liquor is made up in concentrations averaging 80 g. of NaOH per liter. It contains about 10% soda ash from the uncausticized portion of the chemical from the recovery process. The soda ash serves no useful purpose in the cook, but, since its reduction would be expensive, it is carried as an inert load.

(2) *The Cooking Cycle*

The cook is carried on in unlined steel digesters. The amount of liquor added is kept at a minimum volume to facilitate liquor recovery, but sufficient chemical must be added to complete the reaction. The charge of chemical will vary with the species, but will amount to 25–28% NaOH on the weight of the dry wood (20–22% Na_2O). While bringing the cook to temperature, air is relieved from the digester several times to prevent false pressure, and to prevent degradation of the cellulose by oxygen in presence of alkali. Cooks are usually controlled by pressure with the top ranging from 80 to 110 lb./sq. in. Top pressure will be reached in 1 to 2 hrs. and maintained for 4 to 6 hrs. depending on the level maintained. Pulp is blown into tanks and washed in trays or over cylinder washers to recover the liquor at the highest possible concentration.

(3) *Recovery of Chemicals*

The liquor is evaporated to 50–60% solids, at which concentration it will burn if properly atomized in a hot firebox. The organic fraction is consumed in the combustion, steam is recovered from the furnace, and the inorganic chemical as sodium carbonate is run from the furnace in a molten state. The liquor is regenerated to sodium hydroxide with lime, and reused in cooking. Chemical losses in the process, amounting to about 200 lb. of Na_2CO_3 per ton of pulp produced, are made up with commercial soda ash before the liquor is recausticized.

(4) *The Pulp*

The pulp as blown from the digester is a light grayish-brown color. It is almost always bleached before using, since the paper grades in which it is customarily used are white.

(b) THEORY OF THE SODA PROCESS

The theories of the alkali delignification of wood, as proposed by Brauns and Grimes[60] and by Larocque and Maass,[61] are essentially in agreement. The steps in the process are: first, an absorption at the liquor–lignin interface of sodium hydroxide by the acidic hydroxyl groups on the lignin; second, a chemical combination as the temperature rises between the lignin and absorbed alkali; and third, an alkaline hydrolysis of the assumed lignin-carbohydrate bond at elevated temperature, and diffusion of the sodium lignate from the wood.

Brauns and Grimes[60] point out that "the carbohydrates dissolve very rapidly at the beginning of an alkaline cook and only after about 20% of the nonligneous part of the wood has been dissolved does the lignin start to disperse at an effective rate." They also partition the alkali consumed in the cook as follows: for a total alkali consumption of 16%, about 1.5% is used to neutralize such acid groups as formyl and acetyl, about 4% is used to dissolve the lignin, and the remaining 10.5% is used in dissolution of the carbohydrates except for a small portion held in the pulp by adsorption.

Larocque and Maass[61] found that the alkali dissolution of lignin follows the course of a monomolecular reaction, except for the removal of the last 2% which is much slower. The last fraction is probably the lignin distributed through the cell wall and is less available to the liquor. Through studies of the effect of liquor concentration the reaction rate is believed to be controlled by the absorption of the alkali at the lignin–liquor interface. There is no indication as to whether the combination of the alkali and lignin and the dissolution of the lignin are simultaneous or whether one is slower than the other. The energy of solution of the lignin is 32,000 calories per mole.

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[60] F. E. Brauns and W. S. Grimes, *Paper Trade J.*, **108**, 40 (Mar. 16, 1939).

[61] G. L. Larocque and O. Maass, *Can. J. Research*, **19B**, 1 (1941).

5. The Kraft (Sulfate) Process

(a) DESCRIPTION OF THE PROCESS

Certain features of the kraft or sulfate process are discussed below. A complete description of this process and also of the equipment may be found in the literature.[62,63]

(1) The Cooking Liquor

Kraft cooking liquor differs from soda liquor primarily in its sodium sulfide content. The amount of sulfide is expressed in terms of "sulfidity"[64] which is defined as the Na_2S content divided by the sum of the Na_2CO_3, NaOH, Na_2S contents, all expressed as Na_2O. (In this discussion all cooking chemicals will be expressed in terms of Na_2O according to the usage of the kraft industry.) A typical kraft cooking liquor with all chemicals expressed as grams of Na_2O per liter would contain:

NaOH	70 g./liter
Na_2S	30 g./liter
Na_2CO_3	20 g./liter

In the terms of the industry this would be:

Total	120 g./liter (NaOH + Na_2S + Na_2CO_3)
Active	100 g./liter (NaOH + Na_2S)
Sulfide	30 g./liter (Na_2S)

The sodium carbonate fraction, as in the soda liquor, is present as an inert load. It is kept to an economic minimum in the recausticization of liquor. The sulfidity of the liquor is most generally maintained between 25 and 28%. This is a decrease from 33% formerly recommended.

(2) The Cooking Cycle

Since an alkaline liquor will penetrate into wood faster than an acid one, and since higher temperatures can be used with alkali without damaging cellulose, kraft cooks can be much shorter than sulfite. Pulps for paper-

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[62] G. H. Tomlinson, II, and J. N. Swartz, in J. N. Stephenson, editor, *Pulp and Paper Manufacture*, Vol. 1, McGraw-Hill, New York, 1950, Chapter 5; J. P. Casey, *Pulp and Paper*, Vol. I, Interscience, New York-London, 1952, pp. 133–177.

[63] F. G. Sawyer, W. F. Holzer, and L. D. McGlothlin, *Ind. Eng. Chem.*, **42**, 756 (1950)

[64] Tech. Assoc. Pulp Paper Ind., *Standards*, **O 400 p-44** (Aug., 1944).

board can be cooked in as little as 90 min. Pulps for paper are cooked in 2 to 6 hrs. In this country cooks are usually on the short side of the range; those in Europe on the long side.

In the kraft cook only enough chemical is added to complete the reaction. This requires about 15% active chemical ($NaOH + Na_2S$) based on the dry weight of the wood. Limited chemical addition acts as a cooking control and also minimizes the load in the chemical recovery. If more volume of liquid is required to distribute the chemical and the heat, a sufficient quantity of black or spent liquor is added.

Even with the more rapid penetration of alkaline liquors there should be a penetration period of at least 1.5 hrs. If cooking rate becomes appreciable before penetration is complete, the outside of the chips will consume more chemical then necessary, and the centers will not have enough. The resulting pulp would be a mixture of overcooked and undercooked wood. Air is relieved from the digester during the penetration period as in the soda cook.

Maximum cooking temperatures for kraft are most commonly in the range of 170–175°C. (100–115 lb./sq. in.). The cook is retained at this maximum until the desired degree of pulping is attained, pressure is relieved quickly to about 80 lb., and the cook is blown into a tank.

(3) *The Recovery of Chemicals*

The pulp is separated from the weak black liquor on cylinder washers and is then screened before use, as in the case of sulfite pulp. The weak black liquor containing about 10% solids (60% organic, 40% inorganic) is concentrated in multiple-effect evaporators to about 58% solids. At this concentration it is steam-atomized into a hot furnace, where it flash dries and then burns. Air is carefully controlled so that all sulfur compounds are reduced to the sulfide. The molten chemicals run from the furnace and are dissolved in water to make "green" liquor containing Na_2CO_3 and Na_2S. The green liquor is treated with lime to causticize the carbonate. The lime mud is settled out leaving "white" liquor which is returned to the digester. In modern kraft mills the lime mud is reburned to regenerate the CaO. Chemical make-up is with salt cake (Na_2SO_4) added to the furnace with the black liquor so that the sulfate is reduced to the sulfide. Depending on the equipment used and general efficiency, the make-up will run from 100 to 250 lb. of salt cake per ton of pulp made. Efficiencies expected in a well-run kraft mill are:

Chemical recovery	90%
Reduction of sulfur compounds	90–95%
Causticization	85–90%

Steam recovered in modern equipment is sufficient to cook the pulp, evaporate the black liquor, supply the heat necessary in the liquor making, and have a small excess.

(4) *The Pulp*

Kraft pulp is brown in color—the familiar brown of grocery bags. It is the strongest pulp made from wood, and now that it can be bleached successfully it is displacing sulfite pulp where more strength is desirable in white papers. Probably the largest use for kraft in point of tonnage is in the paperboard field for manufacture of corrugated or solid fiber cartons. Here its lower cost and lighter weight have brought about the displacement of practically all wooden boxes. Kraft pulp, being tough, utilizes more power in the beating in preparation for papermaking, and the fibers tend to be less broken down so that special care must be taken in better paper grades to eliminate a coarse surface. Kraft pulp is not yet as satisfactory for dissolving pulps as is sulfite, because removal of hemicelluloses by purification is more difficult. An acid prehydrolysis prior to cooking has produced pulps with much higher alpha-cellulose and in the next few years kraft pulp may invade even the dissolving pulp field.

(b) PROGRESS OF THE COOKING PROCESS WITH TIME

The work of Bixler[30] on pulping thin wood sections and following the lignin removal with staining techniques included kraft. It was noted that the intercellular material was removed completely before the lignin in the secondary walls was attacked. This seems confirmed by the fact that although sulfite will easily produce a pulp with only 1% lignin, reduction of lignin to as far as 2% with kraft is done only at the expense of ruinous loss in pulp yield. Since the sulfite process attacks the secondary cell wall before all lignin in the middle lamella is removed, this process is sometimes considered less specific in lignin removal than kraft. However, high-yield cooks of kraft show that up to 20% of the carbohydrate material will be removed before appreciable quantities of lignin dissolve. As an explanation of the behavior of kraft liquor, the theory is proposed that the well-known swelling effect of alkali on cellulose blocks the penetration of the liquor into the cell wall and retards the removal of the last traces of lignin.

Kimble[65] has followed the development of color and changes in chemical composition of kraft liquor during the cook. Figure 5 taken from Kimble's work illustrates these changes during a cook with the specifications:

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[65] G. C. Kimble, *Paper Trade J.*, **115**, 37 (July 16, 1942).

Wood	Spruce (*Picea mariana*)
Active alkali	20%
Sulfidity	33%
Water: oven-dry wood ratio	5.5:1
Maximum temperature	170 °C.
Time to maximum temperature	1.5 hrs.
Time at maximum temperature	4 hrs.

The following yield data were obtained:

Total yield	46.0%
Screened yield	45.7%
Lignin in screened pulp	3.5%

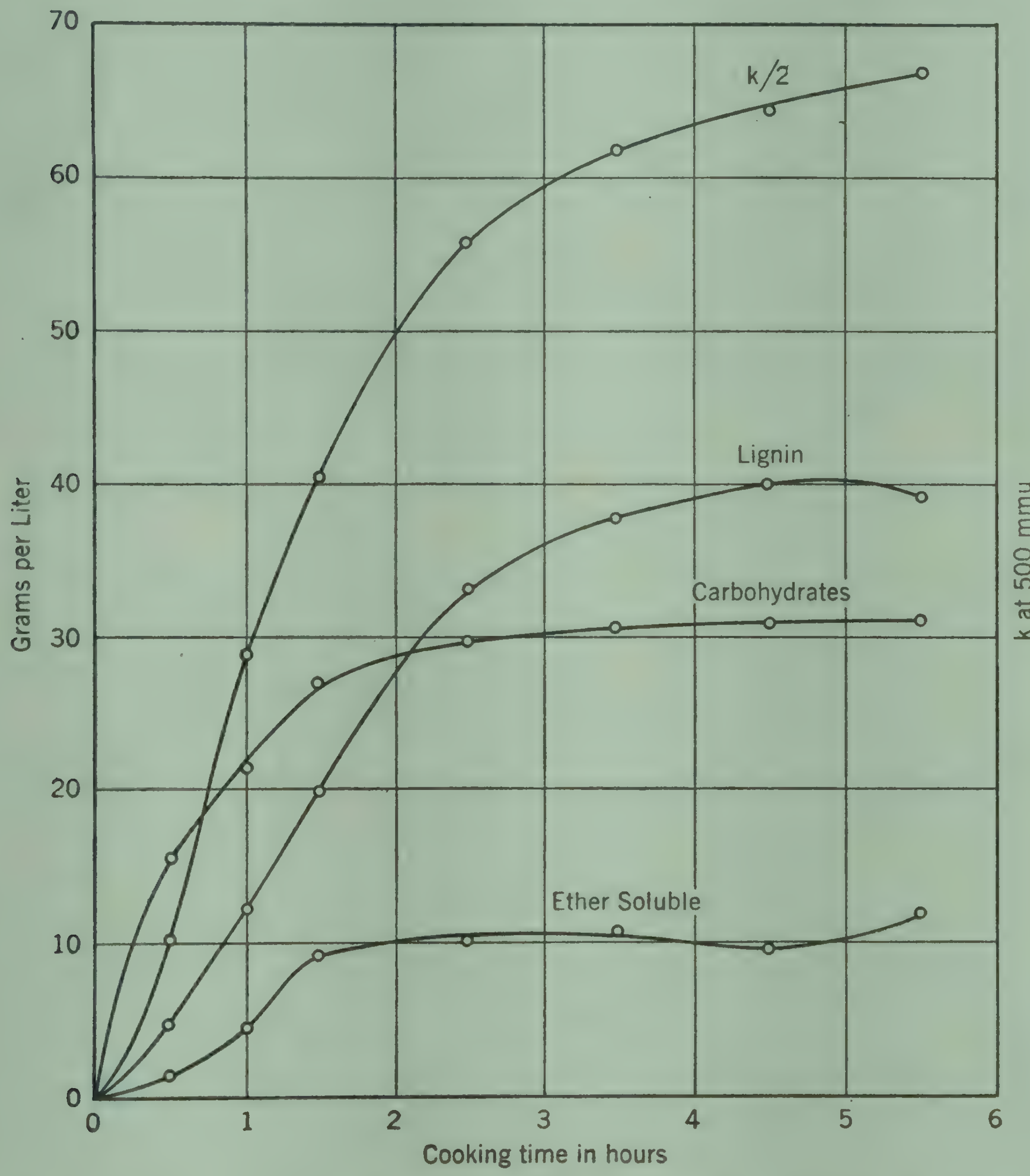

Fig. 5. The concentration of chemical components and coloring matter in sulfate black liquor as a function of cooking time (Kimble[65]).

Kimble found that by far the greatest proportion of the color in kraft black liquor was developed from the lignin. The carbohydrates contributed nothing to the color. The rate of extraction of carbohydrates during the first 2 hrs. of the cook, however, is much faster than the extraction of the lignin.

(c) THEORY OF THE KRAFT PROCESS

When sodium sulfide is added to sodium hydroxide the rate of pulping with the resulting liquor is greatly increased. Figure 6 from the work of Hägglund[66] shows quantitatively the increase in rate of lignin removal. The greatest change in rate is found in the range of low sulfidities. Reduction of time required to reduce lignin in wood to 10% is very close to 50% in going from a soda liquor to a kraft liquor with 31% Na_2S.

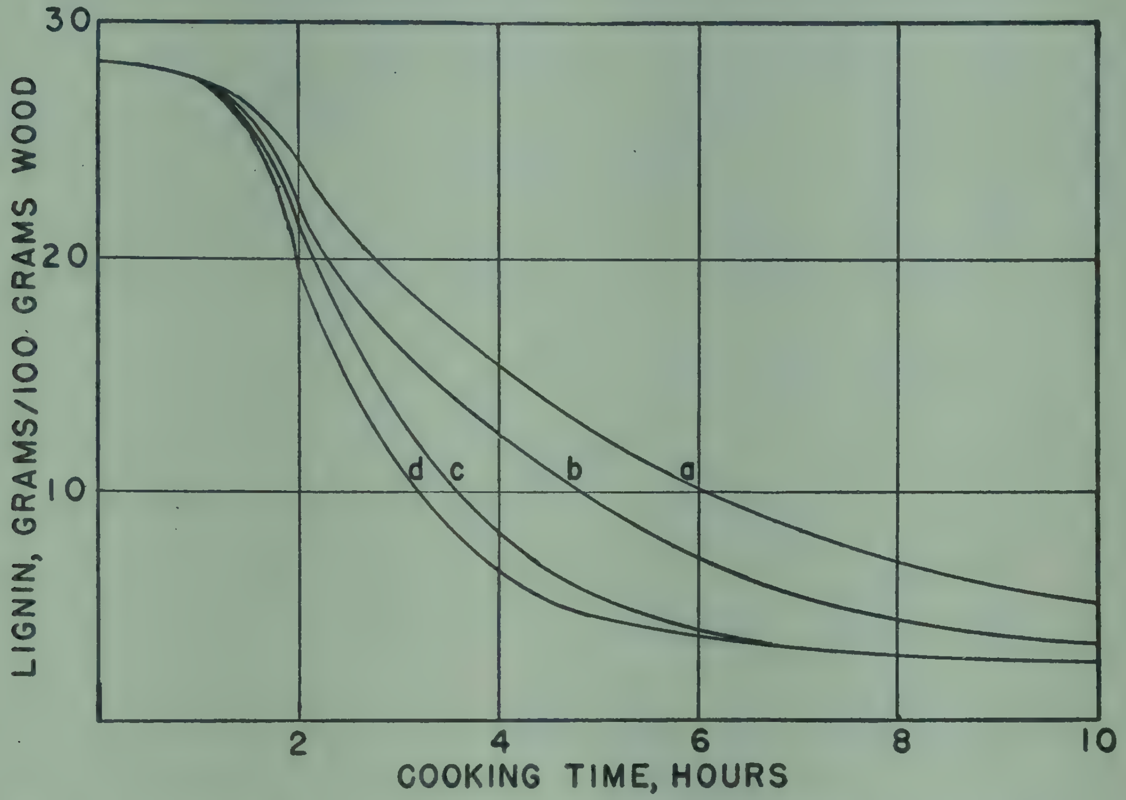

Fig. 6. Increase in rate of alkaline digestion of wood with the sulfidity of the liquor (Hägglund[66]). (a) 0% Na_2S, (b) 5.25% Na_2S, (c) 15.6% Na_2S, (d) 31% Na_2S. Maximum temperature, 160°C.

Further work by the same investigator compares rate of lignin and carbohydrate removal from wood in comparable cooks (Fig. 7). The rate of carbohydrate removal by the two liquors may be considered identical. In the case of lignin, however, the action of the kraft liquor is more rapid from the start, and even after three-quarters of the lignin has been removed, the reaction is proceeding at an only slightly diminished rate. The dissolution of lignin by soda liquor, on the other hand, has almost stopped after less than half has been removed. These two graphs are very significant in the discussion of the theory of the reaction.

[66] E. Hägglund, *Tappi*, **32**, 241 (1949).

The earliest theory for the behavior of the sulfide in kraft liquor was that it acted as a buffer, hydrolyzing to form NaOH and NaHS as the NaOH was consumed. In this way the wood was never subjected to the full concentration of NaOH. Although it has been demonstrated that this hydrolysis takes place,[67] it has long since been recognized that this buffer action has slight effect on the kraft process. The comparative rate of solution of carbohydrates in a kraft and a soda cook is supporting evidence. The presence of sulfur in kraft lignin was recognized early, but it was not until later that its significance was recognized. Hanson[68] found sulfur

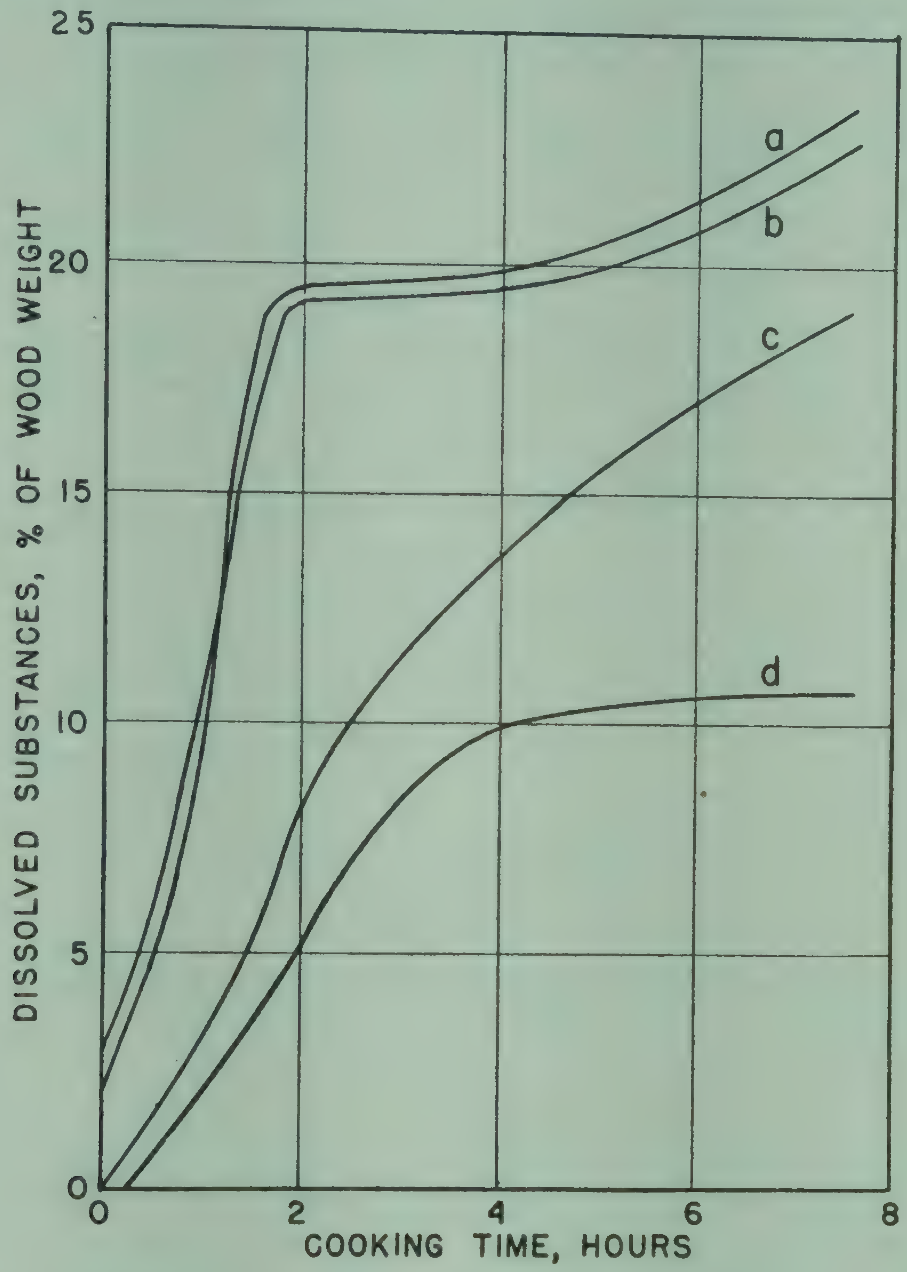

Fig. 7. Comparative rate of dissolution of carbohydrates and lignin during a soda and a kraft cook (Hägglund[66]). (a) Carbohydrate, kraft cook; (b) carbohydrate, soda cook; (c) lignin, kraft cook; (d) lignin, soda cook. Maximum temperature, 140°C., attained in 1.75 hrs.

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[67] G. E. Martin, *Tappi*, **33**, 84 (1950).

[68] F. S. Hanson, *Paper Trade J.*, **112**, 32 (Jan. 9, 1941).

contents of thiolignin (kraft lignin) up to 10%, and proposed that sulfide speeds up the kraft cook by rendering the lignin molecule more acid and thus more soluble in alkali. Ahlm[69] postulated that sulfur in thiolignin was present in the mercaptan form, and that it had added at a carbonyl group on the lignin. Hägglund[66] has objected to both of these theories on the basis that he cannot find any mercaptan sulfur in thiolignin, and that there are not enough carbonyl groups in lignin to account for the sulfur content found in thiolignin. As a result of a long series of researches he proposes the hypothesis that lignin first takes up sulfur in the solid phase, presumably by replacing a hydroxyl group with a mercaptan group. This is not stable in alkali, and is converted to a sulfide by reacting with another hydroxyl either in the same or another lignin molecule. The second step consists of a hydrolytic splitting under the effect of alkali to form free phenolic hydroxyl groups, thus rendering the lignin soluble in the alkali.

The effect of the sulfur is apparently twofold. It is probable that the hydrolytic splitting of the phenolic groups takes place much more easily if sulfur has first reacted with lignin; and second, it is also probable that the sulfidization blocks a condensation-sensitive group, thus preventing the formation of larger, less soluble lignin complexes. Both of these actions of sulfur probably assist in the more rapid dissolution of lignin as shown from the start of the cook (see Fig. 7), and the blocking of lignin condensation accounts for the sustained rate of reaction of the kraft cook as compared to the decrease in lignin removal in the soda cook after condensation has had an opportunity to take place.

(d) COLOR OF KRAFT PULP

Since the first sulfur dyes were produced by heating organic material with sodium sulfide, it was originally assumed that the color of kraft pulp was caused by sulfur dye formation in the cook. Schwartz, McCarthy, and Hibbert[70] found that the color was due to lignin and its degradation products. Bard[71] produced colors similar to kraft pulp by cooking alpha pulp in kraft liquor with tannins and short-chain carbohydrates. Since black liquors from digestions with and without sodium sulfide gave similar spectral absorbencies, sulfur dye formation, if any, cannot be the cause of kraft pulp color. Kimble[65] found in studies of black liquor that 80–90%

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[69] C. E. Ahlm, *Paper Trade J.*, **113**, 115 (Sept. 25, 1941).

[70] H. Schwartz, J. L. McCarthy, and H. Hibbert, *Paper Trade J.*, **111**, 30 (Oct. 31 1940).

[71] J. W. Bard, *Paper Trade J.*, **113**, 29 (Sept. 18, 1941).

of the color was due to lignin. Pigman and Csellak[72] pointed to lignin as the primary source of kraft pulp color. The brightness of the pulp was a direct function of lignin content.

(e) THE EFFECT OF COOKING VARIABLES ON KRAFT PULPS

There have been many publications describing the effect of one or more variables of the kraft cook on the resulting pulp. Most of these results were obtained by keeping all conditions constant except the single variable studied and, as a result, producing series of pulps with varying degree of delignification. Most comparisons of pulps must be made at the same degree of delignification to be valid, and therefore most published data on this subject must be studied with extreme care. Hart and Strapp[73] made a comprehensive survey of the variables in the kraft process, and from their data pulps may be compared at constant degrees of delignification.

The Effect of Sulfidity. At constant effective alkali ($NaOH + {}^1/_2\ Na_2S$) there were marked changes from 0 to 20% sulfidity, slight changes from 20 to 40% sulfidity, and little change thereafter. The changes noted were: cooking time and yield were decreased, physical strength was increased, and chemical constants showed little if any change.

Variations with Maximum Temperature. Screened pulp yield decreased from 48 to 42% on increasing maximum temperature from 160° to 180°C. Burst and tensile were slightly higher and tear lower for the lower temperature. Alpha-cellulose and pentosan showed no change with lower cooking temperature, but viscosity was higher.

Chemical Charge. Screened yield was higher at higher chemical charge, but the reverse was true of burst. Tear showed no consistent trend. Alpha-cellulose content was slightly higher at higher charges, but pentosans and viscosity were lower.

Chemical Concentration. Bray, Martin, and Schwartz[74] have made a study of the effect of chemical concentration over a wide range, and found best results at 50 g./liter. Most commercial liquors are made at double this concentration, but in use are diluted nearly to the preferred range by black liquor or condensate from direct steam, or both.

(f) BY-PRODUCTS FROM THE KRAFT PROCESS

Probably a major share of the kraft pulp produced is made from one or another of the various species of pines. The large amounts of extractives in these woods yield recoverable amounts of by-products.

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[72] W. W. Pigman and W. R. Csellak, *Tech. Assoc. Papers*, **31**, 393 (1948).

[73] J. S. Hart and R. K. Strapp, *Pulp & Paper Mag. Can.*, **49**, No. 3, 151 (1948).

[74] M. W. Bray, J. S. Martin, and S. L. Schwartz, *Paper Trade J.*, **109**, 29 (Nov. 2, 1939).

Turpentine in amounts of 2 gal. per ton of pulp can be recovered by passing the relief gases through a condenser, running the condensate through a decanter, and collecting the turpentine from the overflow.

The extractives in pine will dissolve in the alkaline liquor, and will cream from black liquor after it has been concentrated to half its volume. The skimmings can be collected by decantation in amounts of 150–200 lb. per ton of pulp. The crude soaps are treated with sulfuric acid to form a dark oil known in the trade as "tall oil." Tall oil consists of a mixture of resin acid, fatty acids, and unsaponifiables.[75] The first two comprise over 90% of the total, and are present in fairly equal amounts. The resin acids are substantially the same as those in American wood rosin[76]; the fatty acids are linoleic, linolenic, and oleic; and the unsaponifiables are lignoceric alcohol and sterols, principally phytosterols.

During World War II the shortage of fats led to extensive studies on tall oil and to its introduction into many industries some of which are: soap, emulsion, detergent, flotation, adhesives, paint and varnish, and printing ink.[77]

6. Other Pulping Processes

(a) NEUTRAL SULFITE

The neutral sulfite process has come into some prominence in the last ten years as a method of producing high-yield pulps from hardwoods. This process in its present form was first proposed by Rue and coworkers[78] in 1927. It consisted of cooking wood with about 15% of its weight of Na_2SO_3 with sufficient $NaHCO_3$ present to neutralize the acids formed during cooking. The action was so mild that delignification was incomplete, and best results were obtained on hardwoods, since their lignin content was lower than that of softwoods.

The process was very little used for several years, but the growing scarcity of softwoods in the Great Lakes and New England sections, together with increasing stands of hardwoods, forced the use of the latter in pulping, and brought the neutral sulfite method to the fore.[79] At first its use was to make a high-yield pulp for board, but now several mills are bleaching the high-yield hardwood pulp, and are obtaining a papermaking fiber. Bleached neutral sulfite hardwood pulp has strength nearly equal to softwood sulfite pulp, and replaces the latter in many papers. Yields of pulp run from 55 to 60% for a bleached papermaking fiber to 80% for board.

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[75] T. Hasselstrom, *Paper Trade J.*, **118**, 30 (Apr. 20, 1944).

[76] G. C. Harris, *Tappi Monograph Series*, No. **6**, 167 (1948).

[77] National Southern Products Co., *Tappi*, **33**, 76A (Jan., 1950); 58A (Feb., 1950).

[78] J. D. Rue, S. D. Wells, F. G. Rawlings, and J. A. Staidl, *Chem. & Met. Eng.*, **34**, 611 (1927); *Tech. Assoc. Papers*, **10**, 90 (1927).

[79] M. W. Phelps, *Northeastern Wood Utilization Council Bull.*, **14**, 59 (Jan., 1947).

(b) PREHYDROLYSIS OF WOOD

During World War II the need for dissolving pulps in Central Europe became acute, but no cotton linters and very little softwood pulps were available. Beechwood, which like all hardwoods is high in pentosans, became the principal raw material. A process of prehydrolysis[80] was devised to render these pentosans soluble. The wood chips were subjected to an acid treatment at high temperatures (160–180°C.) for a short time (15–60 min.), and this pretreatment was followed by an alkaline cook. The pretreatment could be merely a cook in water, the acids in the wood doing the hydrolyzing; or a small amount of mineral acid, hydrochloric or sulfuric, might be added. After bleaching, pulps of 95% alpha-cellulose or higher were obtained. Pulps made by the prehydrolysis process are already a considerable factor in the American dissolving pulp market.[81] It is anticipated that this process will be used to an even greater extent in the near future.[82]

(c) OTHER PROCESSES

Suggestions for methods of pulping of wood have been legion, but few have survived outside of the laboratory. Many modifications of the established processes, principally multistage cooks, have been tried, but the time consumed, heat lost, chemicals used, or equipment required in the complications have made them impractical. Many chemicals have been tried ranging from strong acids, such as nitric, to bases both organic and inorganic, to neutral organic solvents, such as alcohols and glycols, to hydrotropic solvents, such as xylene sulfonates, to name a few. None of these has as yet shown sufficient merit in quality of pulp or in cost to compete with the established processes. Some have been of theoretical interest, but aside from the two mentioned in preceding paragraphs, none has achieved any commercial production.

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[80] G. Sirakoff, *Holz Roh- u. Werkstoff*, **4**, 205 (1941); through *Chem. Abstracts*, **38**, 2201 (1944).

[81] Anon., *Pulp & Paper*, **24**, 66, 92 (Nov., 1950); *Paper Trade J.*, **132**, 11 (Apr. 6, 1951).

[82] Anon., *Paper Trade J.*, **134**, 41 (Feb. 1, 1952); 11 (Mar. 14, 1952).

7. Properties of Pulps and Their Constituents Affecting End Use

The many variables in the pulping processes plus the inherent differences in various wood species can be combined in an almost infinite number of combinations to produce a varied assortment of pulps. The properties of these pulps depend on their content of lignin, cellulose, and hemicelluloses, on the condition of these constituents, and on the dimensions of the fibers themselves.

The principal requirement for a pulp as a chemical raw material is a high content of alpha-cellulose with almost complete removal of lignin and extractives, and substantial reduction of hemicelluloses. This will be discussed fully elsewhere in this volume (see Chapter VII).

The properties of papers will depend on the degree to which the fibers will adhere to each other, the ultimate strength of the fibers, the dimensions of the fibers, and on the relative stiffness or softness of the fibers.

Lignin. The stated purpose of pulping was to remove lignin, and generally a low lignin content is necessary. In a very raw pulp the lignin remains as a sheath enveloping the fiber. Since it does not swell in water itself, hinders the swelling and hydration of the cellulose in the fiber, and makes the fiber very stiff, lignin is usually detrimental to paper quality. Sheets made from such fibers are harsh and low in strength. On the other hand, it is desirable to leave as much lignin in the fiber as can be tolerated since its complete removal entails considerable loss and degradation of cellulose. In certain instances the presence of lignin is desirable. In paperboard it contributes stiffness to the product, and in hardboard (a wallboard finished at high temperatures under extremely high pressures) it acts as a resin, making the product extremely hard and dense.

Hemicelluloses. This fraction is of considerable importance in papermaking. In the process of beating, where the fibers are bruised and rubbed in a water suspension, the hemicelluloses absorb water, swell, and become gelatinous. During the beating this gel coats the fibers; and when the fibers are formed into a web, and the web is pressed and dried, the hemicellulose gel acts as an adhesive, and cements the fibers into a strong sheet. As a general rule, the greater the hemicellulose content is, the faster the pulp will respond to beating, the harder and denser will be the resultant paper, the higher will be its bursting strength and tensile strength, and the greater will be its transparency. The extremes of paper grades illustrating these differences are facial tissue having fibers low in hemicellulose, with soft feel and little bonding; and glassine and greaseproof papers needing the highest possible amount of hemicellulose to produce a very dense, hard sheet with good transparency. In between are such grades as paper towels, blotting, and soft-type printing papers on the soft side, wrapping papers in the medium range, and strong bond papers on the hard side.

Cellulose. Some of the discussion of cellulose has already been anticipated. The presence of cellulose itself in a fiber in undegraded form is no assurance that a paper will be strong. Pure cellulose is quite soft and has poor

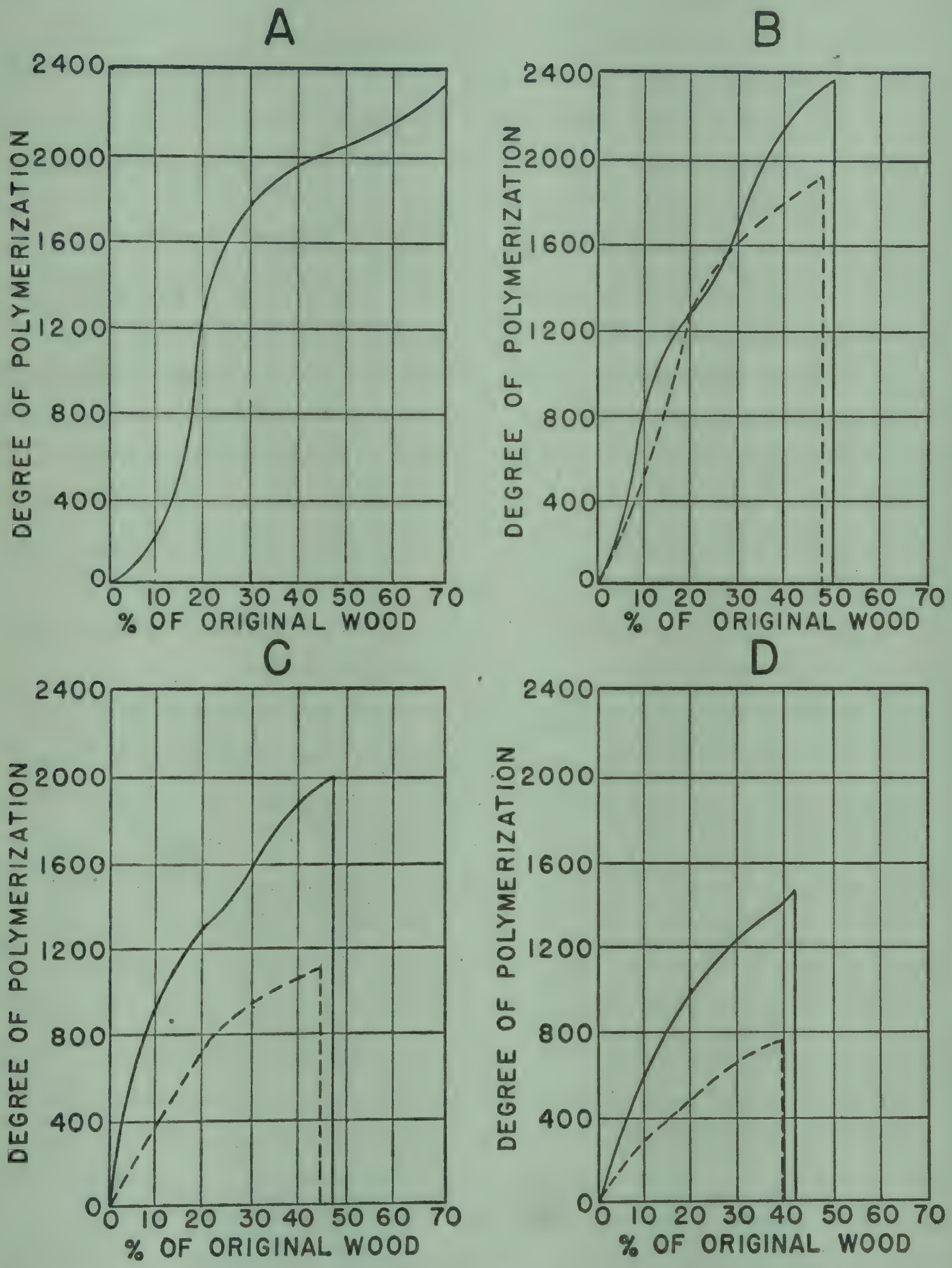

Fig. 8. Degree of polymerization of the carbohydrate fraction of (A) sprucewood holocellulose, (B) sulfite pulp, (C) kraft pulp, and (D) soda pulp (Atchison[83]). Curves are shown for both unbleached (solid line) pulps and bleached (dotted line) pulps. Holocellulose and all pulps were prepared from the same wood sample.

B. COTTON LINT AND LINTERS

A. F. MARTIN

Cotton is the only plant seed fiber or seed hair to attain major commercial importance. It is one of the most important raw materials for textiles and is an important source of chemical cellulose for conversion into derivatives. Raw cotton consists almost entirely of cellulose, with minor amounts of waxes and pectins being the chief contaminants.[1] Lignin is not present in appreciable amounts. Other seed hairs such as kapok and milkweed floss are discussed briefly in Chapter II-D-2.

1. Types of Cottonseed Fibers

Two types of hair, lint fibers (or staple cotton) and linters, are found on the usual varieties of cotton seed (Fig. 9). These fibers are removed from

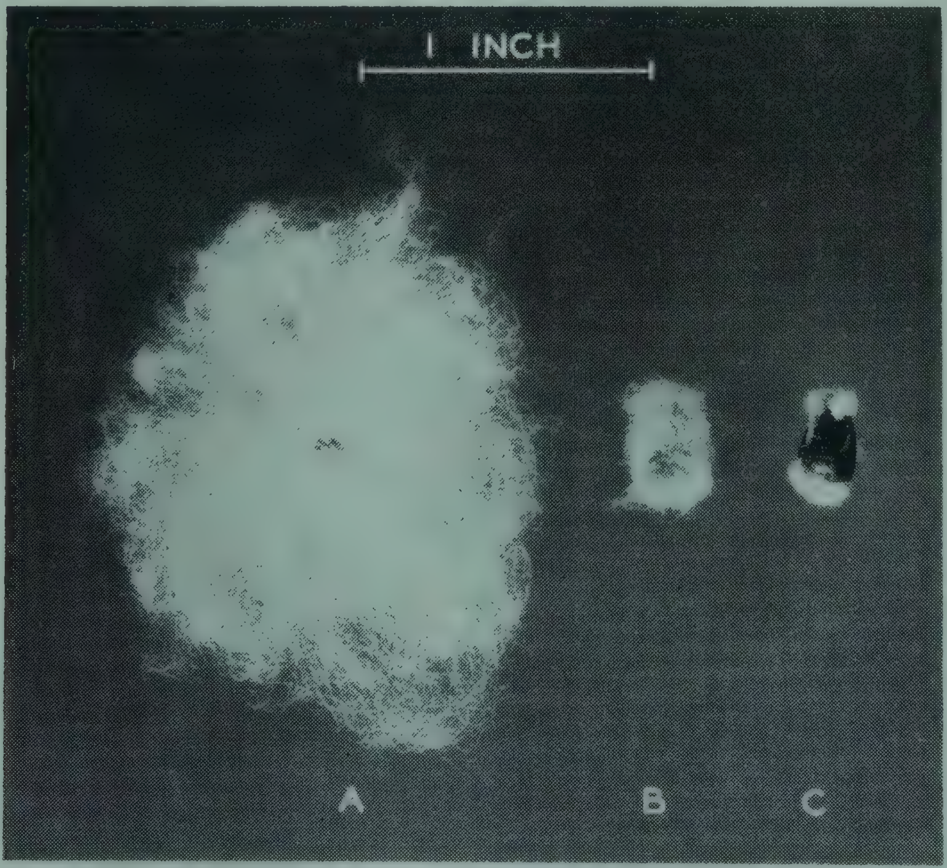

Fig. 9. Cotton seeds with fibers: (A) seed with all fibers (lint and linters); (B) seed with linters after removal of lint; (C) seed with hull fiber after removal of linters. Courtesy of Hercules Powder Company.

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[1] J. H. Kettering and C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **14,** 432 (1942).

fiber-to-fiber bonding qualities. This will produce paper of the soft type such as facial tissue. On the other hand good bonds from hemicellulose cannot make a strong sheet unless they are complimented in the fiber with strong cellulose. In general, cellulose contributes tearing resistance to paper, and when present in nearly pure form will make a permanent sheet.

The condition of the carbohydrate fraction after various cooking and bleaching treatments makes an interesting comparison. Atchison,[83] by fractional solution methods, developed D.P. curves of the holocellulose of sprucewood, and of the sulfite, kraft, and soda pulps, both bleached and unbleached. His data are summarized in Figure 8. The curve for wood holocellulose shows an appreciable fraction of very short-chain hemicelluloses, relatively little of the medium-length chains, and the bulk of the material with chain lengths of D.P. 2000 and over. The curves for sulfite and kraft show the great decrease of the short-chain material, the presence of considerable amount of medium-length chains resulting from degradation of the longer chains, and the very appreciable loss of long-chain material. Greatest loss in short-length chains is found in the soda pulp, and the extreme degree of degradation is evident. The relative yield of each carbohydrate product is shown by basing the abscissas of the graphs on the extractive free wood. By comparing the yields along with the shape of the distribution curve, the magnitude of the over-all degradation becomes apparent. The further degradation on bleaching is shown in the respective dotted curves.

Fiber Dimensions. The approximate fiber sizes and variations in cell walls have already been described. The length of softwood fibers, about 3–4 mm., is generally too long for good forming properties, and reduction of this length is one of the objects of the physical treatment a pulp receives before the papermaking process. The small fiber fragments mat together into a smoother sheet, and being smaller, present more surface for contact with each other and therefore more bonded strength. If the reduction process is carried too far the ultimate strength of the fragments will be less than that of the bonds, and the paper strength will drop correspondingly.

Pulping of wood and making paper from these pulps has long been looked upon as an art. The discussion of the field has indicated the degree to which the technical men have reduced it to a science. However, with the variations of a natural raw material, plus the infinite combinations among the variables of the processes, and the gaps of our knowledge, it seems that the complete success of science is still some distance in the future.

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[83] J. E. Atchison, *Paper Trade J.*, **116,** 23 (June 3, 1943).

the seed in two separate operations. The staple cotton is the major product and comprises about half the weight of the seeds which are taken from the boll of the matured cotton plant. This staple cotton is removed from the seeds in mills or gins of which there are about 8000 in the United States. The machines used in this operation are also called gins and consist primarily of a bank of rotating circular saws. The seeds after the ginning operation are sent to cottonseed oil mills which delint (that is, remove linters from) the seeds and crush them to recover cottonseed oil and meal. There are about 400 oil mills in the United States.

The most important difference between lint fibers and linters is in fiber length. Nevertheless, the two types of hair differ also in diameter, degree of collapsing of the central canal, and other features (see Chapter IV-C). Lint fibers have a length of over 2 cm. and are used primarily in textiles because they can be spun into thread possessing high tensile strength. The shorter linter fiber are used form attresses, upholstery, and similar products and especially for the preparation of pure cellulose ("chemical cotton") which is used in the manufacture of derivatives.[2–5]

Several types of linters can be produced by modification of the operation of the cottonseed oil mill. Mill runs are made by removing the majority of the linters from the seed in one operation. They have a number-average fiber length of about 3 mm. and are quite nonuniform. More frequently the linters are removed in two or more passes through the delinting equipment[6] (Fig. 10A). The first-cut linters average 6–12 mm. in length and the second-cuts average about 2 mm. A small amount of fiber remains on the ends of the cotton seed after the usual delinting operation and is sometimes recovered from the hulls after the seeds are crushed. This product, known as hull fiber, differs from the other cottonseed fibers in that it is usually produced by abrading the fibers from the pieces of hull in machines such as the Reynell-Ware defibrator[7] (Fig. 10B). Hull fiber may have a length equal to second-cut linters but is usually somewhat shorter. An additional small amount of fiber known as "delint" is obtained from some of the seeds which are to be planted to furnish the next season's cotton crop.

[2] W. D. Munson, *Ind. Eng. Chem.*, **22**, 467 (1930).

[3] G. D. Bieber, *Chem. & Met. Eng.*, **48**, 92 (Jan., 1941).

[4] E. F. Hinner, *Chemurgic Digest*, **4**, 179 (1945).

[5] J. Barsha and P. VanWyck, in R. E. Kirk and D. F. Othmer, editors, *Encyclopedia of Chemical Technology*, Vol. 3, Interscience, New York-London, 1949, pp. 352–357.

[6] W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed*, Eng. Expt. Sta., Univ. of Tennessee, Knoxville, 1935, p. 51.

[7] C. H. Reynell and A. J. V. Ware (to Reynell-Ware Inc.), U. S. Patent 2,004,731 (June 11, 1935).

In addition to fiber length, color and degree of contamination are two important factors in determining the utility of cottonseed fibers. The color of lint fibers will vary from white to yellow to gray, depending on the species of cotton and the degree of exposure of the fibers after the boll has opened. Raw linters are usually olive or buff, although a large proportion of the apparent color may come from the contamination which is present. The foreign matter in both lint and linters will include seedcoat fragments; pieces of stalk, leaf, and boll from the cotton plant; other plant materials; and sometimes sand and dust. Both the cotton gins and the cottonseed oil mills commonly use seed-cleaning equipment as well as fiber-cleaning equipment in order to upgrade the fibers. The seeds are usually cleaned with shaker screens; the fibers, with machines called cards or beaters.

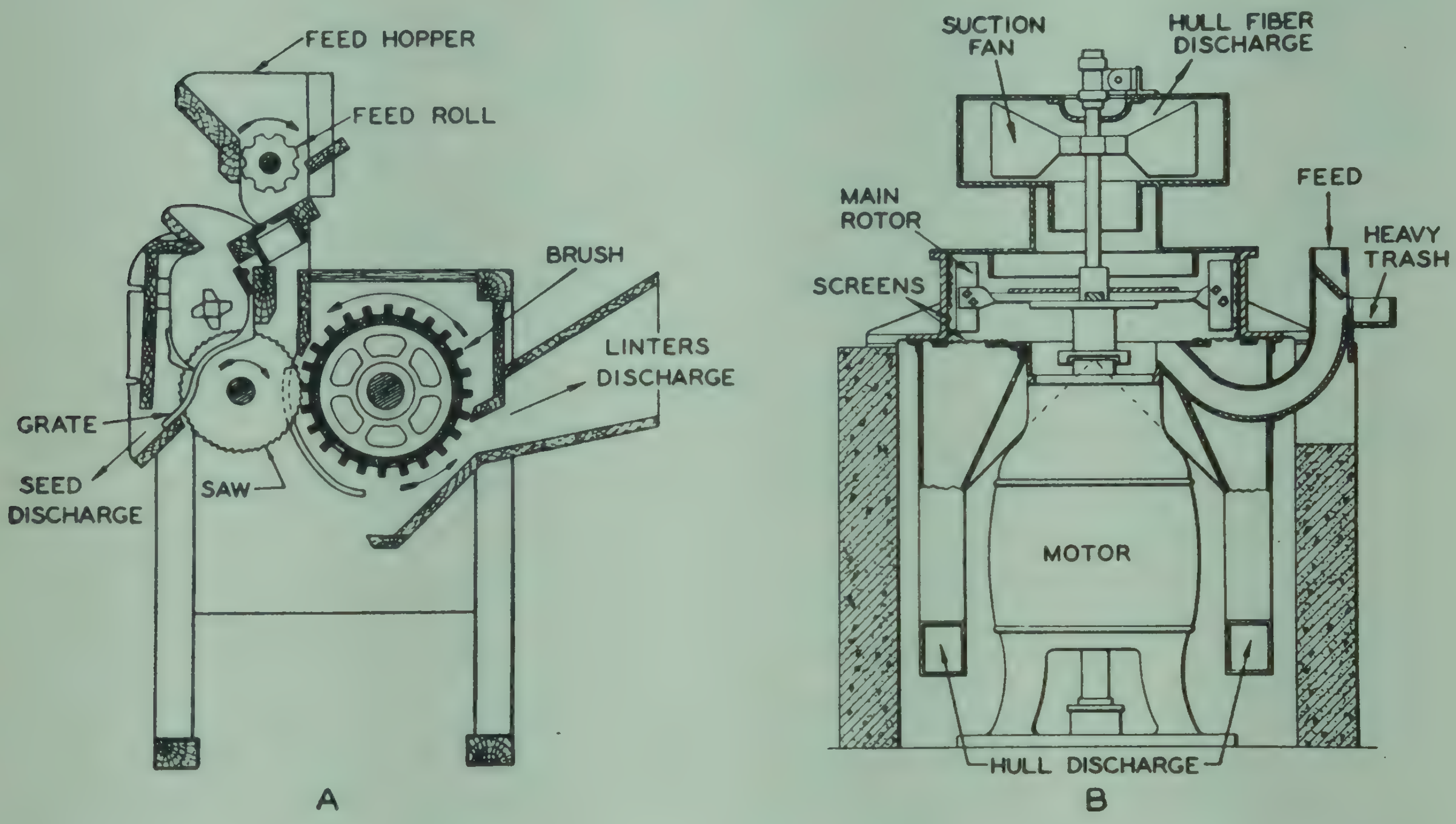

Fig. 10. Linters production equipment. (A) Delinter[6]: Linters stripped from the cotton seeds by the saws are doffed by the more rapidly moving brush roll. (B) Defibrator[7]: Linters are abraded from the hulls against the vertical screen by centrifugal force set up by the main rotor. The heavier hulls fall through the bottom screen, while the lighter linters are carried inward and upward by the air stream.

Standards have been set up for grading and classifying cottonseed fibers on the basis of fiber length, color, and extent of contamination. The official U. S. Department of Agriculture methods involve subjective comparison of the fiber samples with standards.[8] For grading American upland cotton, there are nine classifications which relate to degree of contamination and amount of waste, and six classifications which relate to color. The fiber length is described by one of twenty classifications between 0.75 and 1.5 inches. The linters standards are similarly divided into seven grades, with chief emphasis on fiber length and color.[9,10] Grades 1 to 4 represent the longer first-cut and mill-run linters; Grades 5 to 7 represent second-cuts and hull fiber.

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[8] U. S. Dept. Agr., *Misc. Pub.* **310** (1938).

For linters fibers which are to be used to make chemical cotton, the subjective grading methods of the Department of Agriculture are not sufficient. The development of additional objective tests is a goal of the American Oil Chemists' Society. Of those developed to date, the most widely used is the "pot yield" method[11] which determines the amount of cellulose which can be obtained from a given weight of raw cotton linters. The results of this test are used in determining the price of second-cuts and hull fiber, with premiums being paid for yields above 73% and deductions made for yields below 73%. A test for cotton linters contaminants is also under consideration.[12] Fiber length is relatively unimportant in chemical cotton except as it affects the design of equipment to process the cellulose into derivatives.

2. Economics of Utilization of Cottonseed Fibers in the United States

In the last ten years, the cotton production in the United States has varied from about 9 to about 16 million bales per year[13] (Table 2). Sales prices in this ten-year period have ranged from 11 to 40¢/lb., so that U. S. cotton is frequently a billion-dollar annual crop.[14] Cotton is grown in all of the southern states from North Carolina to California. The center of production is shifting from the Southeast, where small farms are the rule, to Texas and California,[15] where the economies of large-scale production mean

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[9] U. S. Dept. Agr., Bur. Agr. Econ., *Service and Regulations Announcement*, **94** (1925).

[10] G. S. Meloy, U. S. Dept. Agr., *Misc. Pub.* **242** (1936).

[11] L. N. Rogers, *Oil & Soap*, **14**, 199 (1937); **22**, 24 (1945).

[12] T. L. Rettger, *Oil & Soap*, **22**, 7 (1945).

[13] U. S. Dept. Agr., Bur. Agr. Econ., *Statistical Bull.* **99** (1951), p. 5; Supplement (1952), p. 11.

[13a] U. S. Dept. Commerce, Bur. Census, *Cotton Production in the United States—Crop of 1952*, Washington (1953), p. 2.

[14] U. S. Dept. Agr., Bur. Agr. Econ., *United States Cotton Statistics*, Washington (1951), p. 2.

[15] *Ibid.*, p. 1.

greater profits. Nevertheless, acreage controls, support prices, and government loans are all used to protect the marginal high-cost cotton producer. These controls have modified the operation of the economic laws of supply and demand.[13]

TABLE 2

Production of Cotton in the United States[13,13a]

Year beginning Aug. 1	Acreage harvested (in thousands of acres)	Production (as thousands of 500-lb. bales)
1940	23,861	12,566
1941	22,236	10,742
1942	22,602	12,820
1943	21,610	11,429
1944	19,617	12,230
1945	17,029	9,016
1946	17,584	8,640
1947	21,330	11,857
1948	22,911	14,868
1949	27,439	16,128
1950	17,843	10,012
1951	26,687	15,144
1952	—	15,137

The high price of cotton has been a large factor in the growth of the synthetic fiber industry, which in turn has furnished intense competition for cotton. In 1949 the textile industry consumed 28% as much synthetic fiber as it did cotton.[16] Both acetate and viscose rayon as yarn can now be sold at prices below that for cotton yarn.[17] This situation can exist only when the price of chemical cellulose is far below the price of cotton textile fibers. Second-cuts and other cottonseed fibers are used in rayon to the extent that availability and price will allow.

Cotton linters are recovered in amounts of about 180 pounds per ton[18] of the seeds processed in cottonseed oil mills. They are a by-product in that their sales value is less than that of cottonseed oil and meal[19] (Table 3).

[16] *Textile Organon*, **23**, 40 (1952).

[17] *Textile Organon*, **23**, 37 (1952).

[18] U. S. Dept. Agr., Production and Marketing Administration, *Weekly Cotton Linters Review*, **22**, No. 5 (Aug. 31, 1951).

[19] Compiled from figures given in: U. S. Dept. Agr., Bur. Agr. Econ., *Statistical Bull.* **99** (1951), p. 368; U. S. Dept. Agr., *Agricultural Statistics*, Washington (1951), p. 125; various issues of U. S. Dept. Agr., Production and Marketing Administration, *Weekly Cotton Linters Review*.

TABLE 3

Gross Sales Value of Cottonseed Products in the United States[19]

Year beginning Aug. 1	Sales value in millions of dollars		
	Cottonseed oil	Cottonseed meal	Linters
1940	93.2	52.1	27.4
1941	153.4	64.2	33.5
1942	178.6	75.4	37.6
1943	157.6	89.0	31.7
1944	168.8	94.8	34.2
1945	129.8	79.0	—
1946	241.1	161.2	57.8
1947	334.9	164.7	52.8
1948	262.8	151.4	39.9
1949	229.9	160.7	58.6
1950	242.2	128.7	115.8

Nevertheless, since the profit margin in oil and meal may be comparatively small, linters sales are of great importance to the oil mills. The amount of linters, being a function of the size of the cotton crop, will vary from year to year. In addition, the demand for chemical cellulose has shown an unusually large growth rate. The result is that in several periods the total amount of chemical cellulose including wood pulp has been insufficient to supply the demand, and linters prices have risen sharply.[20] Because of planned expansions in the wood pulp industry and an apparent leveling-off in demand for rayon, it is expected that prices will remain fairly stable at reasonably low levels for the next several years.

The bleaching establishments which transform second-cut linters into chemical cotton follow the policy of purchasing raw linters only upon receipt of a binding contract for finished chemical cotton. The operators of the bleaching establishments have a threefold function. As bankers, they finance the purchase of raw linters and are repaid on delivery of the chemical cotton. As warehousers, they store up to a full year's supply of raw linters. Finally, as manufacturers, they transform raw linters into the custom-made types of chemical cotton.

3. Cottonseed Fibers in Other Countries

The United States produces about one-half of the world's supply of cotton.[21] As shown in Table 4, other countries producing more than a million bales a year are U.S.S.R., India, Egypt, China, Brazil, and Pakistan. Of these countries, China, India, and Pakistan produce only small quantities of linters, primarily because transportation is insufficient to support a cottonseed oil industry. The strains of cotton grown in Egypt have no linters on the seed, that is, the seeds are "bald."[22] The production of linters outside the United States is therefore limited chiefly to Brazil, Mexico, U.S.S.R., East Africa, and Paraguay.

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[20] U. S. Dept. Agr., Production and Marketing Administration, *Weekly Cotton Linters Review*, **19**, No. 29 (Feb. 18, 1949); **21**, No. 38 (Apr. 20, 1951); **23**, No. 13 (Oct. 23, 1952).

TABLE 4

Production of Cotton in Principal Cotton-Growing Countries[21] for Year Beginning August 1, 1949

Country	Production (as thousands of 480-lb. bales)
United States	16,800
U.S.S.R.	2,700
India	2,300
Egypt	1,796
China (including Manchuria)	1,700
Brazil	1,385
Pakistan	1,000
World total, including all other countries	31,190

Linters purification plants have in the past been installed close to the large users of chemical cotton. Thus, England, Germany, France, Italy, and Japan have bleaching establishments which depend entirely upon importation of linters. The trend, however, is toward purification of linters in the countries in which they are grown. Currently, the consumption of chemical cotton in Europe and Japan is so great that the United States bleaching establishments export sizable quantities to these areas.[23]

4. Linters Purification

All the cottonseed fibers may be purified by similar means, even though the equipment for carrying out the purification will vary depending on the fiber length. The bales of lint cotton are broken up and mechanically cleaned at the textile mills but usually undergo no other purification until after they have been spun into yarn or woven into cloth. The subsequent purification process usually consists of a desizing operation, an alkaline boil, and a hypochlorite (or peroxide) bleach with thorough washing to remove the remaining bleaching solution.[24]

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[21] U. S. Dept. Agr., Bur. Agr. Econ., *Statistical Bull.* **99** (1951), pp. 128–129.

[22] *American Cotton Handbook*, American Cotton Handbook, Inc., New York, 1941, p. 128.

[23] U. S. Dept. Commerce, Bur. Census, *U. S. Exports of Domestic and Foreign Merchandise*, Report No. **FT410**, Part 1, 13 (Nov., 1951).

The transformation of linters into chemical cotton demands an unusual amount of quality control and will be described in detail.[25–29] The chemical operations involved in purification of raw linters are pressure digestion in alkaline liquors, and multistage bleaching. The sequence of steps is similar to that used in wood pulping by the soda process (see Chapters VI-A and VII), but the exact conditions employed are different because of the differences in the types and amounts of impurities which must be removed and in the physical form of the raw cellulosic material. Linters purification steps are primarily designed to remove wax, pectins, and small amounts of coloring matter which are distributed on or in the fiber, and at the same time to destroy almost completely the contaminants which are physically dispersed in but separate from the linters. In addition, the purification steps regulate such important chemical cotton properties as viscosity and reactivity.

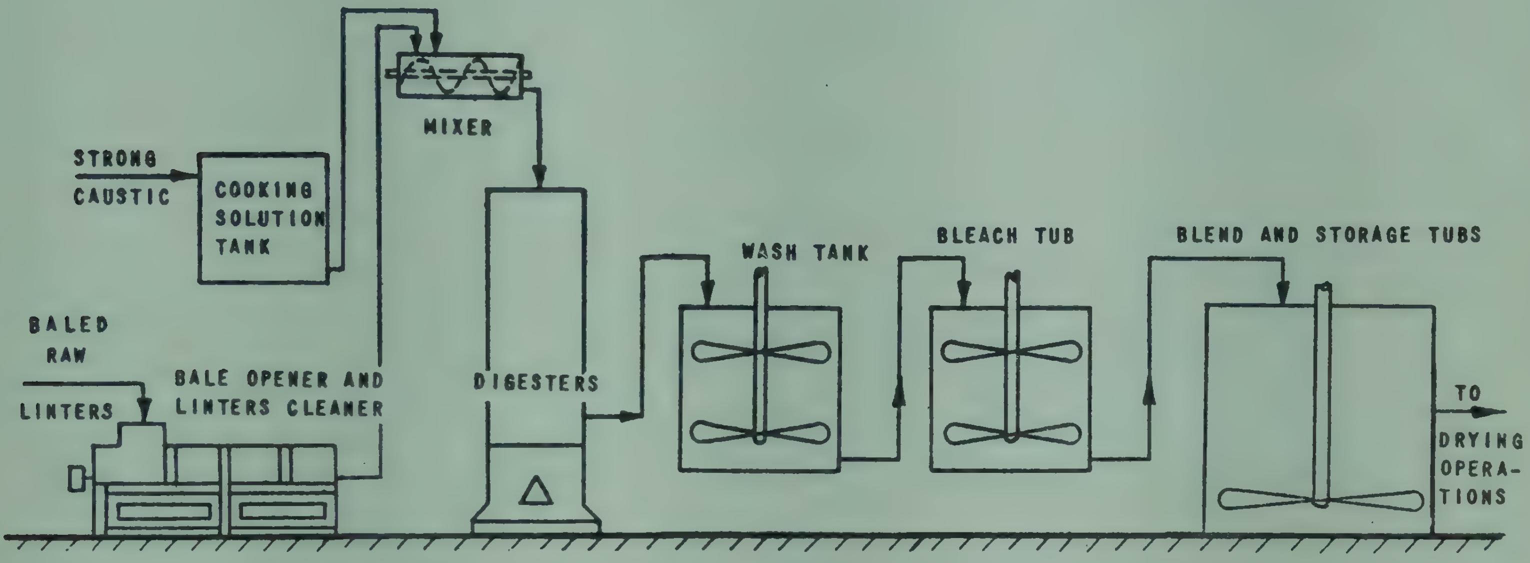

Fig. 11. Linters batch purification process. Courtesy of Hercules Powder Company.

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[24] J. H. Kettering and R. M. Kraemer, U. S. Dept. Agr., *Tech. Bull.* **941** (1947).

[25] J. A. Lee, *Chem. & Met. Eng.*, **48,** 90 (Apr., 1941).

[26] *Chem. & Met. Eng.*, **48,** 108 (Apr., 1941).

[27] *Hercules Chemical Cotton*, Hercules Powder Co., Wilmington, Del., 1947, 35 pp.

[28] *Bukipulp*, Buckeye Cotton Oil Co., Memphis, Tenn., 1949, 40 pp.

[29] *How Chemcot Is Custom Made to Your Specifications*, Southern Chemical Cotton Co., Chattanooga, Tenn., 24 pp.

The raw linters contaminants include particles of boll, stalk, leaf, and the palisade-cell layers of hull which are quite resistant to the usual chemical treatments. In addition, somewhat larger quantities of the epidermal layer of the cottonseed hull (called "hull pepper" or "hull bran") are present in raw linters but are more easily removed in the purification steps. The loss of hull pepper is a major reason for the drop in yield during purification.

Batch equipment is commonly used to perform the purification steps (Fig. 11), but recently a completely continuous process[30] has been installed in one of the bleaching establishments.

(*a*) *Selection of Raw Linters*

The amount of contamination in raw linters is one of the major factors influencing the quality of chemical cotton and the uses for which it may be sold. Both the quantity and type of contamination will vary widely in linters from different cottonseed oil mills and even in the production from a single mill. The bleaching establishments rely upon the experience of highly skilled inspectors to purchase enough high-quality raw linters to make chemical cotton within specification.

Representatives of the bleachers go to almost every cottonseed oil mill to sample the production and to approve individual bales for shipment. Often the inspectors advise the oil mills as to the quality needed for the chemical industry and suggest methods of obtaining larger quantities of satisfactory linters from the seeds. The response of the oil mills to the need for improved quality has been good, and present quality levels are high compared with those of a few years ago.

Each carload of inspected linters is further tested at the purification plant. In many cases, this testing may include a complete laboratory-scale purification. After testing, the linters are segregated and stored according to the grades of chemical cotton in which they may be used. As expected, the larger the stock of raw linters, the better is the opportunity for selection so that uniform satisfactory quality levels may be maintained in all grades of chemical cotton.

The quality level of raw linters can be improved to some extent by mechanical cleaning operations in the bleaching establishment. Equipment which separates contaminants from linters by centrifugal action on a water slurry[31] is now in commercial operation. Beaters, screens, and other apparatus may be used to clean dry linters.[32,33]

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[30] W. E. Segl (to Hercules Powder Co.), U. S. Patent 2,673,690 (Mar. 30 1954); *Chem. Eng.*, **61**, 116 (1954).

(*b*) *Digestion*

The bales of raw linters are usually disintegrated by mechanical opening equipment as a first step in the purification process. When mechanical cleaning treatments are used, they are applied after the bale opening and prior to digestion. For digestion, the opened linters are wetted with sodium hydroxide solution of the required strength (usually 2 to 4%) and are transported to the digesters. Digestion factors such as time, temperature, and concentration of alkali must be balanced to get the desired degree of cellulose purification and the desired level of final viscosity. Wetting agents are often added in small amounts to the digestion liquors to aid in removing impurities.[34] Continuous digestions are reported to be carried out in times as short as 10 min. and at temperatures as high as 185°C.[30] Batch digestion, either in vertical stationary digesters or in rotating or tumbling digesters, is usually carried out at 135–170°C. for 2 to 6 hrs. Even though the pressure treatment is carried out in the absence of air, cellulose is degraded by the contact with hot alkali. Severe digestion conditions result in loss of yield and loss of viscosity.

After digestion, the spent liquor ("black liquor") must be removed by efficient washing operations. In batch processing this is done by displacement in false-bottom tubs, an operation which is feasible because of the rapid draining characteristics of the cotton linters. Countercurrent continuous vacuum washers[35] are rapidly coming into favor because they use less water and consequently minimize dilution of the black liquor.

The black liquor contains most of the soluble organic materials which are removed from linters during the purification process. This liquor may be evaporated and burned as is done in the wood pulping industry (see Chapter VI-A). Recovery of the caustic soda used in digestion is a part of this operation. The economics of black liquor recovery require minimum dilution for profitable operation.

[31] J. D. Atkinson (to Buckeye Cotton Oil Co.), U. S. Patent 2,504,944 (Apr. 18, 1950)

[32] A. J. V. Ware, U. S. Patent 2,210,016 (Aug. 6, 1940).

[33] A. K. Schwartz and F. J. Walker (to South Texas Cotton Oil Co.), U. S. Patent 2,239,059 (Apr. 22, 1941); A. K. Schwartz, E. Bradshaw, and F. J. Walker (to South Texas Cotton Oil Co.), U. S. Patent 2,274,385 (Feb. 24, 1942); *Chem. Abstracts*, **36**, 4354 (1942).

[34] E. K. Bolton (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,048,775 (July 28, 1936); *Chem. Abstracts*, **30**, 6210 (1936).

[35] *Filters for the Process Industries*, Bull. 214, Oliver United Filters, Inc., New York, 8 pp.

(*c*) *Bleaching*

As a result of the digestion step, the linters have been freed from most of the contaminating substances but are still tan in color and generally require bleaching treatments. Viscosity, reactivity, and other properties may be further adjusted during bleaching. Time, temperature, pH, and concentration of bleach are the important factors in the bleaching operation. It is customary to use multistage treatment with a sequence of steps similar to that employed in wood pulp purification (see Chapter VII). The active bleaching agents may be chlorine, hypochlorite, chlorine dioxide, peroxides, permanganate, and other oxidizing agents, although the first two are most frequently used. The bleach requirements for cotton linters are so low that excess reagents must generally be added in order to get a sufficiently high concentration to exert a bleaching action. It is, therefore, not usually possible to employ the common wood pulping practice of using less than the bleach demand in order to prevent attack on the cellulose. Special precautions must be taken in linters bleaching to prevent or to regulate cellulose degradation.[36]

The bleaching treatments must be carefully controlled and coordinated with selection of raw linters and with digestion[37] so that the finished product specifications for such factors as color, viscosity, and cleanliness may be met. Because these specifications vary from grade to grade, the bleaching procedures cannot be standardized. Custom bleaching is the usual practice.

Batch bleaching is generally done in large, well-agitated, stainless steel-lined tubs. Interstage washing is carried out in the same tubs, and the liquors are drained off through false bottoms. Cotton bleaching is also carried out in continuous equipment similar to that of the wood pulp industry. Both low-consistency and high-consistency towers are used, while washing is accomplished on rotary table filters. All the bleaching equipment is constructed of corrosion-resistant materials because contamination of the purified cellulose must be avoided.

The bleaching operation also includes in many cases a treatment with sulfuric or other acids to act as souring agents and to reduce the ash content. Sequestering agents and chemicals such as oxalic acid are also often used to remove metal ions in the final purification steps.

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[36] A. M. Dodson (to Hercules Powder Co.), U. S. Patent 2,478,379 (Aug. 9, 1949); *Chem. Abstracts*, **43**, 9447 (1949).

[37] L. M. Sheldon (to Cellulose Research Corp.), U. S. Patent 2,190,274 (Feb. 13, 1940); *Chem. Abstracts*, **34**, 4267 (1940).

(*d*) *Drying*

Before drying, the purified chemical cotton is usually submitted to further mechanical treatments such as riffling[38] or centrifuging, in order to remove siliceous[39] or other foreign matter which was not removed by chemical treatment.

Chemical cotton is usually dried and packaged in sheet form for the viscose, cellulose ether, and paper trades, and in loose form for most other uses (Fig. 12). The temperature and time of drying have in general a great influence on the physical form of the finished product and its reactivity. Careful drying is, therefore, of the utmost importance.

The first step in drying in loose form is dewatering the slurry by screens and rubber-covered squeeze rolls to a moisture content of approximately 50%. The pads of chemical cotton from the squeeze rolls are fed through pickers revolving at high speed which put the linters in a fluffy form.[40] A layer of fluffed linters on a metal apron is carried through a tunnel dryer. Air of carefully controlled temperature and moisture content is blown through the cellulose layer. The dried cotton is baled, weighed, and wrapped in kraft paper in readiness for release for shipment. Loose pulp bales usually average about 180 lb. with a moisture content of about 5%.

Conventional fourdrinier papermaking equipment is used to dry chemical cotton in sheet form. Jordan engines are used to reduce the fiber length so that a smooth, strong sheet can be obtained. Careful adjustment of this cutting treatment is necessary to get uniform sheet properties. As in the case of loose pulp, sheet pulp is dried at controlled temperatures. The thickness, density, formation, and porosity of the sheet may be regulated over wide ranges to fit the requirements of each customer. For some uses, the continuous sheet from the machine is cut, stacked, and baled; for other uses, the sheet is wound onto rolls of specified width. The bales generally weigh 400 lb.; the rolls may weigh as much as 600 lb.[27]

Chemical cotton for acetylation use is generally dried at low temperature (60° to 80°C.) in order to retain reactivity. Overdrying must be particularly avoided. Cotton for papermaking is often dried to a high moisture content. The other grades of chemical cotton are usually less critical in regard to drying conditions, but a uniform product must always be obtained.

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[38] W. E. Henry (to Hercules Powder Co.), U. S. Patent 2,394,378 (Feb. 5, 1946); *Chem. Abstracts*, **40**, 6815 (1946).

[39] A. Langmeier (to Hercules Powder Co.), U. S. Patent 2,576,464 (Nov. 27, 1951); *Chem. Abstracts*, **46**, 1257 (1952).

[40] W. E. Segl (to Hercules Powder Co.), U. S. Patent 2,516,262 (July 25, 1950).

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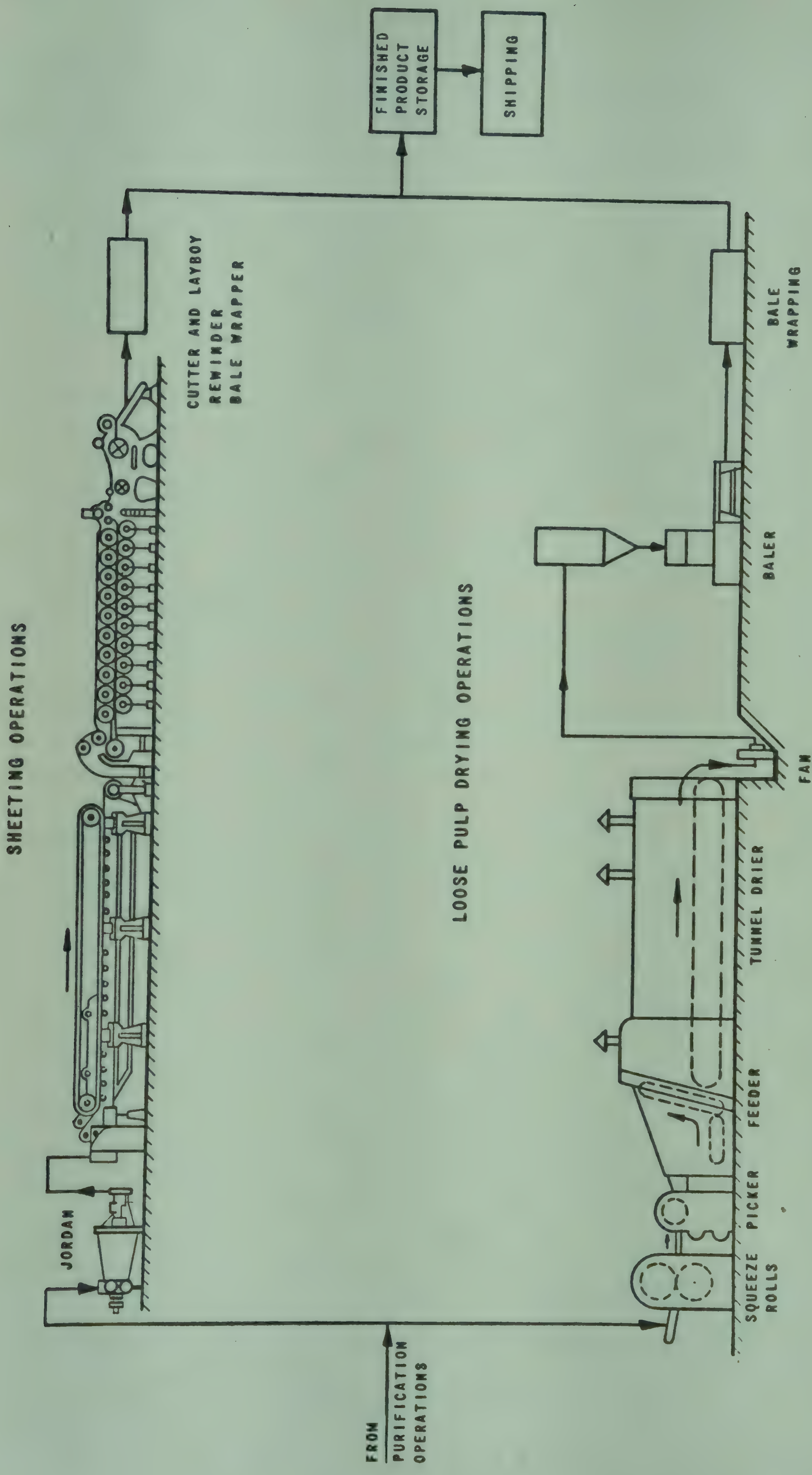
SHEETING OPERATIONS
JORDAN
CUTTER AND LAYBOY
REWINDER
BALE WRAPPER
FINISHED PRODUCT STORAGE
SHIPPING
LOOSE PULP DRYING OPERATIONS
SQUEEZE ROLLS
PICKER
FEEDER
TUNNEL DRIER
FAN
BALER
BALE WRAPPING
FROM PURIFICATION OPERATIONS

Fig. 12. Chemical cotton drying operations. Courtesy of Hercules Powder Company.

(*e*) *Analysis*

The different grades of chemical cotton and the narrow specifications for these grades require careful analytical control at every stage in the purification process.[27] The analytical work begins with raw linters and includes "pot yield" determinations, small-scale purifications, and visual inspection. The digestion liquors are analyzed for alkali strength, and the digested linters are tested for such properties as viscosity and cleanliness. At each stage in the bleaching operation, viscosity and cleanliness will again be measured and other tests will be employed. As might be expected, a complete analysis is made of the finished, dried chemical cotton so as to make sure that the requirements of the customer are met. In many cases, the final analysis includes the small-scale preparation of derivatives such as the acetate and viscose. Such use tests are especially valuable in predicting how the chemical cotton will behave in the customer's manufacturing operations. (The details of the commonly used cellulose tests may be found in Chapter XII.)

5. Uses for Chemical Cotton

Chemical cotton has achieved outstanding success in the preparation of those derivatives in which good clarity, freedom from color, and high strength are of importance.[2–5,27,28] This success is due in large part to the exceptional purity of cotton cellulose as distinguished from cellulose obtained from other sources. In addition, chemical cotton is almost always the standard cellulose which is used for the preparation of new cellulose derivatives. However, since chemical cotton is not available in large enough quantities to fill all needs, wood pulp is frequently substituted in the manufacture of established derivatives up to the extent that quality requirements will permit. Chemical cotton, therefore, finds widest uses when the good strength, color, clarity, and fiber properties which it can contribute are essential to the finished product.[41]

(*a*) *Viscose and Cuprammonium Rayon*

The largest present use for chemical cotton is in the manufacture of high-tenacity rayon by the viscose process (see Chapter IX-F). The strength of tire cord from chemical cotton, especially under the severe heat and stress encountered in motor vehicle operation, is outstanding. The recent commercial development of the prehydrolysis–sulfate wood pulping process[42]

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[41] C. J. Malm, *Svensk Papperstidn.*, **50**, No. 11B, 135 (1947).

[42] *Pulp & Paper*, **24**, 66, 92 (Nov., 1950); *Paper Trade J.*, **132**, 11 (Apr. 6, 1951)

(see Chapter VI-A) is expected to cause keen competition for chemical cotton in high-tenacity rayon. This development is an indication of the dynamic nature of the chemical cellulose industry and of the constant need for improvement if present markets are to be kept or new markets obtained.

Chemical cotton is also the preferred raw material for conversion by the viscose process into extruded sausage casings. High wet strength is the necessary property in this use. In the viscose textile rayon industry, chemical cotton was displaced by wood pulp almost 20 years ago because of the availability of the latter raw material.

Chemical cotton finds wide use in the cuprammonium rayon industry, which specializes in strong, fine yarns. The spinning process, which depends on drawing down thick (0.5–1.0 mm. diameter) filaments to low deniers, can take advantage of the high strength contributed by chemical cotton.

(*b*) *Cellulose Esters*

The exceptionally good color obtainable from chemical cotton has made it the base for cellulose acetate and nitrate which are to be used in clear or pastel plastics. Photographic film, whether acetate or nitrate, is generally made from chemical cotton in order to have good clarity. In rayon uses, chemical cotton, when used as a portion of the cellulose furnish, is said to contribute to ease of spinning and to strength of yarn.

Chemical cotton is widely used in the manufacture of nitrocellulose explosives. It is the preferred raw material for rocket powder. Because it can be furnished at very high viscosity levels, it is the only chemical cellulose used in the manufacture of dynamite.

(*c*) *Cellulose Ethers*

As in the case of cellulose esters, chemical cotton is used in the manufacture of ethers where color, clarity, and high viscosity are important. In these alkaline manufacturing processes, chemical cotton with its low caustic-soluble content has distinct advantages in yield as compared with wood pulp.

(*d*) *Paper and Miscellaneous Uses*

The uses for rags in the manufacture of paper which have developed as a result of the strength, permanence, and brightness of the cotton fibers are described in Section C of this Chapter VI. The diminishing supply of high-quality rags has created interest in the use of purified cotton linters in the paper field.[43] Purified linters do not usually give strengths equivalent to rags when conventional beating conditions are employed, but permanence and brightness are excellent. In many cases, the combination of chemical cotton with bleached sulfate wood pulp will give papers entirely equivalent to the conventional bond papers made from rags and bleached sulfite. Chemical cotton is often added as a part of the paper furnish to give absorbency, bulking value, and good formation.

The high porosity of linters sheets has resulted in the development of numerous specialty uses. Laboratory and commercial filter papers are generally made from chemical cotton. Other chemical cotton papers are impregnated with resins for the manufacture of plastic laminates, floor coverings, and lubricating-oil filters. These specialty applications are expected to be of growing importance in the future.

[43] W. H. Jones, *Paper Trade J.*, **121**, 145 (Sept. 27, 1945); **123**, 29 (Aug. 29, 1946).

C. RAGS

Harry F. Lewis

Cotton and linen rags have long been an important source of cellulose for all uses. In the United States their use has been limited to paper and fiber stock. However, rags have been used in other countries as raw material for cellulose derivatives as well as for paper; for example, various types of new cotton waste were used, in the immediate past, in nitration processes. This discussion will be confined to the utilization of cellulose from rags in this country.

In the earliest period in American history, rags represented almost the only raw material available for the manufacture of paper, and it might be said that the amount of paper produced was controlled by the amount of rags thus collected. Wood pulps produced by the sulfite and sulfate processes have gradually supplanted rags in one type of paper after the other. Today rags are going principally into high-grade bond and writing paper and into ledgers where permanence and durability are of importance, and into blottings, fiberboards, and felts, where absorbency and porosity must be obtained.

As the result of these developments, the amount of rag stock produced and converted into fine paper at first fell off considerably. During the past few years, however, the production of rag-content paper in the United States has again shown an increase—170,110 tons in 1947, as against an estimated 100,000 tons in 1899. These production figures do not mean, however, that rag stock production has increased 70%. The modern papers average 40% rag content because common practice is to dilute rag stock with other papermaking fibers. The earlier papers were 100% rag content.

The rags used for conversion into bleached rag stock, one of the purest forms of cellulose produced technically, may be either new rags or old rags. New rags include bleached cuttings from the textile field, such as light prints, white and fancy shirt cuttings, shoe cuttings, and blue overalls. The old rags are sold under a variety of classifications, being termed old whites, thirds and blues, blue overalls, and the like.

Naturally, these different materials show considerable variation in the noncellulosic impurities which must be removed in the cooking and bleaching processes; hence, there is some variation in processing required to remove these different components. The rags before cooking are sorted, cut, and dusted.

New rags may contain as sizing agents starch, certain synthetic resins, and saponifiable and nonsaponifiable fats and waxes. They may also contain synthetic fibers, including besides the derived cellulose fibers (rayons) such newer fibers as those made from polyamides, polyesters, and acrylonitriles. New rags may be white or dyed. Faster dyes, which are continually being developed, complicate the problem of dye removal. Various resins such as the ureas, melamines, acrylates, and polyvinyls may have been added to impart stiffness, freedom from wrinkling, or other special effect. Rubber and rubber derivatives are often present in knit goods. Old rags contain similar contaminants and frequently also contain inorganic and organic dirt. Many of these noncellulosic substances are removed during the normal pulping processes; however, a sufficient number of the materials cause trouble to warrant avoiding use of rags containing them. In addition, the synthetic fibers are undesirable constituents of rags intended for conversion to paper in that these fibers contribute nothing in the way of strength and may detract from the appearance of the sheet and degrade its physical characteristics.

The cooking chemicals generally used for removing the various impurities or rendering them susceptible to bleaching include lime, lime and soda ash, and caustic soda. Grimm[1] has studied the action of the different alkalies on vegetable and animal fibers and concluded that sodium carbonate in excess works well on vegetable but not on animal fibers, and that sodium hydroxide attacks vegetable fibers, destroys animal fibers, and saponifies waxes, fats, oils, etc.; in contrast, the use of lime results in less degradation of vegetable fibers and at the same time destroys animal fibers and colors. In general, the effect of lime on cellulose is milder than that of an analogous amount of caustic soda; hence, with stocks where the minimizing of degradation is an important factor, lime is used; in this case, the cooking period must be extended. When the pulping agent is either sodium hydroxide or sodium carbonate, the majority of the fatty impurities present go into solution as soluble salts of fatty acids following saponification. Nonsaponifiable hydrocarbons are first emulsified but may recoagulate on the fibers in the beater to appear in the finished paper.

In the presence of vat dyes such as indigo and the indanthrenes, the action of the cooking agent may be extended by the use of strong reducing agents, for example, sodium hydrosulfite ($Na_2S_2O_4$) or the modified hydrosulfites, or milder reducing agents such as the modified starches and simple carbohydrates. Thorough mixing of the hydrosulfite with the rags in the presence of the least possible amount of air, followed by a washing operation to remove the reduced dye, is essential to good stripping of such pigments. These conditions are particularly important in the case of indanthrene-dyed rags.

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[1] H. Grimm, *Zellstoff u. Papier*, 1, 7, 32 (1921).

Laughlin[2] has studied the effect of variables such as time, temperature, and concentration of cooking chemicals on the degradation of cellulose. He showed that a cooking process using 3.5% NaOH or 10% lime carried out for 3 hrs. at temperatures corresponding to 100 to 150 lb. steam would not degrade the cellulose too greatly; conditions in excess of these proved to be harmful, with pressure and chemical concentration having more effect than time.

It is almost impossible to outline any set of conditions as being standard for the processing of these various grades of rags. The amount of cooking chemical used depends on the rag being cooked; white rags take less chemical and time than do colored ones, clean rags less than dirty ones. In the United States, the cooking operation is generally carried out in horizontal boilers having capacities from 5000 lb. to 16,000 lb. or more. Rarely does the caustic used exceed 10% of the weight of the rags nor the lime 20%.

The product obtained from the rag boiler after cooking and washing is generally far from the brightness desired; hence, it is necessary to remove the cooking residues by bleaching. The cooked rags are first washed, generally in a beater equipped with a washing cylinder, in order to remove soluble colored substances or loosened dirt. Lime-cooked rags are generally washed with cold water to take advantage of the greater solubility of lime in cold water. After washing is complete, the roll is lowered, and the cuttings are drawn out to separate them into threads and the threads into fibers. When this stage is achieved, bleach is added. Most rag mills use calcium hypochlorite for the purpose, although other bleaching agents have been proposed, and at least one of the newer ones, sodium chlorite, is said to yield a product of satisfactory color with no degradation of cellulose.

A number of investigations have been made on the effect of the variables of bleaching on the quality of the rag stock produced. Crain[3] has considered in detail the effect of variables such as pH, temperature, and time of bleaching on the chemical constants and physical properties of the

[2] E. R. Laughlin, *Paper Trade J.*, **97**, 39 (Oct. 26, 1933).

[3] R. C. Crain, *Paper Trade J.*, **103**, 37 (Dec. 10, 1936).

bleached pulp. He has shown that, for hypochlorite bleaches between pH 4.85 and 9.5, the maximum degradation as measured by viscosity occurs at or near the neutral point. Degradation also occurs more rapidly with increase in temperature; this is particularly true above 45°C. Crain's work confirms the experiments made by Birtwell, Clibbens, and Ridge,[4] by Clibbens and Ridge,[5] and by Davidson[6] on the action of bleaching agents on cotton to be used for textile purposes. (A detailed discussion of factors affecting bleaching is given in Chapter VII.)

After a satisfactory color has been achieved, the stock is dropped into a drainer with or without washing. Here it evens up in brightness and softens somewhat, possibly due to the degradation which may occur. Inasmuch as in the manufacture of the various grades of rag papers a mixed furnish of stocks of different sources and cooking processes is used, the drainers both improve the color and at the same time provide storage facilities for the different stocks.

The physical and chemical characteristics of the drainer stock will depend upon the quality of the rag before cooking, the severity of cooking and bleaching, thoroughness of washing, and conditions existing in the drainer. The three chemical constants most commonly used to characterize rag stocks are the cuprammonium viscosity, copper number, and alpha-cellulose content (see Chapter XII). Standard methods for carrying out the determinations have been established by the Technical Association of the Pulp and Paper Industry.[7,8,9] Bleached stocks in a good mill will vary in cuprammonium viscosity from 30–40 to 200–400 centipoises, in copper number from 0.1 to 1.5, and in alpha-cellulose from 90 to 98%. Few rag stocks will be obtained having the optimum values in these various ranges; it is not uncommon, however, to see bleached stocks from new rags having a viscosity of 250, copper number of 0.1, and alpha-cellulose content of 97.5%. High-grade new rag stock of this quality will contain principally alpha- and beta-cellulose; rag stock from old rags may contain small amounts of gamma-cellulose.

In view of the fact that high-quality, rag-content papers are widely used where permanence is desired, the nature of the term "permanence" in this connection is of interest. The term is associated with the concept of life expectancy as applied to paper. The life expectancy of a paper may depend on the complex chemical system of the sheet as well as on the external conditions encountered by the sheet during its use or storage. The direct determination of this life expectancy has not been done. It is unfortunate that actuarial statistics are not as easily obtained with paper as with humans and that they do not have the same wide interest; otherwise, permanence might be estimated with some sureness. To make the collection of data more difficult and less probable, the life expectancy of a permanent sheet extends for several centuries and many generations of investigators.

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[4] C. Birtwell, D. A. Clibbens, and B. P. Ridge, *J. Textile Inst.*, **16,** T13 (1925).

[5] D. A. Clibbens and B. P. Ridge, *J. Textile Inst.*, **18,** T136 (1927).

[6] G. F. Davidson, *J. Textile Inst.*, **24,** T185 (1933); **25,** T174 (1934); **29,** T195 (1938); **31,** T81 (1940).

[7] Tech. Assoc. Pulp & Paper Ind., *Standards*, **T 206 m-37** (Sept. 15, 1937).

[8] Tech. Assoc. Pulp & Paper Ind., *Standards*, **T 215 m-38** (Jan., 1938).

[9] Tech. Assoc. Pulp & Paper Ind., *Standards*, **T 203 m-40** (Jan. 15, 1940).

The next best approach is to devise means for accelerating the more important processes of natural degradation so as to obtain relative figures which will in themselves be without absolute value but will enable an estimate of the relative permanence of a number of sample sheets under conditions which are readily reproducible. One such accelerating agent is an increase in the temperature at which the sheet is maintained. The accelerated aging test of the Bureau of Standards[10] is carried out for 72 hrs. in a current of moving air at 100°C. Changes in the chemical composition and physical characteristics of the sheet establish a measure of the permanence of the sheet. Ultraviolet light has been used by a number of investigators as an accelerated aging test, although possibly its greatest use is in obtaining a measure of the color stability of a sheet. (This may be related to the fastness of the dyes used in the sheet furnish.) Wood pulps show wide variation in ultraviolet-light color stability. Any attempt to establish a quantitative relationship between the results obtained by an accelerated aging test and the life expectancy of a paper is not warranted except in terms of the deteriorating conditions specified in the particular accelerated test employed.

The conditions within the sheet which influence its permanence include the acidity of the sheet, the nature and amount of additives and impurities, and the quality of the pulp stock used in the furnish. The pH of the water extract[11] gives a measure of the acidity; this is related to the amounts of papermaker's alum and rosin size used in the manufacturing process. In general, the lower the extract pH, the less permanent is the sheet in terms of the Bureau of Standards test; this is supported by experience with commercial papers. Sheets having an extract pH of 3.0–3.5 may be expected to undergo degradation in a relatively few years even where high-grade rag stocks are used in the furnish. The same papers having an extract pH of 5.0–5.5 will last many more years. This effect is strikingly illustrated by Hanson,[12] who was intrigued by the fact that certain sections in a book printed on rag paper in 1576 were badly discolored and weakened but others were white and sensibly strong. The strong white sheets all had higher calcium carbonate ash (2.5–3.0%) and extract pH value. The weaker sheets had less ash (less than 1%) and showed lower extract pH's. The gradation from white to brown was in direct order with the increase in carbonate ash and the diminution in strength and extract pH of the sheets.

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[10] R. H. Rasch, *Bur. Standards J. Research*, **7**, 1 (1925).

[11] Tech. Assoc. Pulp & Paper Ind., *Standards*, **T 435 m-42** (July, 1942).

The quality of the stock going into the sheet may be measured by the alpha-cellulose content, the cuprammonium viscosity, and the copper number; it may be concluded from studies at the Bureau of Standards and The Institute of Paper Chemistry that the higher the alpha-cellulose content and viscosity of the stock and the lower its copper number, the longer will be the life expectancy of a sheet made from that stock, other things being the same.[13,14] Again, any attempt to establish a quantitative relationship between the results of any of these tests and the life expectancy of the sheet is unwarranted since these results together with the pH do not represent all of the factors in the sheet influencing its permanence. The mechanism of degradation and the resistance of the sheet to degradation are complex and at best are not too clearly understood.

Among the other factors which have been established as causing a sheet to degrade are the sulfur dioxide in the atmosphere,[15,16] metallic residues which catalyze the oxidation of sulfur dioxide to sulfur trioxide,[17] acids and other corrosive material in the inks,[18] fungus attack under favorable conditions of heat and humidity, and the action of hot sunlight at high humidity. Under any of these conditions, the best-made sheet will deteriorate rapidly. The better the sheet, the longer will it withstand such deterioration. Under normal conditions, a sheet of permanent paper will last a long time. For permanent storage of valuable papers, precautions must be taken to maintain optimum conditions of storage with the elimination of degrading light waves and undesirable atmospheric constituents.

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[12] F. S. Hanson, *Paper Ind. and Paper World,* **20,** 1157 (1939).

[13] H. F. Lewis, *Paper Trade J.,* **95,** 29 (Nov. 24, 1932); **96,** 41 (May 11, 1933).

[14] R. H. Rasch and B. W. Scribner, *J. Research Natl. Bur. Standards,* **11,** 727 (1933); **23,** 405 (1939).

[15] A. E. Kimberly, *J. Research Natl. Bur. Standards,* **8,** 159 (1932); U. S. Bur. Census, Vital Statistics, *Special Reports* **3,** No. 33, 153 (1937).

[16] M. S. Kantrowitz and R. H. Simmons, *Proc. Graphic Tech. Conference,* **1936,** 3.

[17] W. H. Langwell, *Tech. Bull., Brit. Paper Board Mfg. Assoc.,* **29,** No. 1, 21 (1952); No. 2, 52 (1952).

[18] M. E. Whalley, "Abstract of Report to League of Nations on the Permanence of Paper," *Paper Trade J.,* **97,** 32 (July 20, 1933).

Often associated with permanence is the term durability. Not all permanent papers are also durable but paper such as currency which will be handled extensively must be both permanent and durable. A permanent paper which is initially strong will generally be classified as durable.

Apart from the use of rag cellulose in the fine papers, large amounts of rags go into the manufacture of felt for later impregnation with asphalt for roofing purposes or impregnation, coating, and printing for floor coverings. The paper used is generally soft and very porous; because a free sheet is desired, the beating process is carried out with a minimum of hydration.

Quantities of rags also find their way into the manufacture of vulcanized fiber, which operation involves the treatment of waterleaf paper, usually made from old rags, with a solution of zinc chloride or with sulfuric acid. For many types of fiber, old rags work better than new rags or wood pulp, although the latter is used to a considerable extent. The virtues of old rags may well lie in their characteristic combination of degradation and oxidation. A number of plies of the treated sheet are combined, and the laminated sheets are passed through successive baths of ever weaker zinc chloride and finally into fresh water. After drying, pressing, and calendering, the material is ready for use in electrical insulation, in the manufacture of luggage and trunk coverings, and for other related applications.

Although for years the principal source of cotton fiber for the manufacture of high-grade paper has been rags, within recent years there has been an increasing use of cotton linters and even the long staple lint cotton (see Section B of this Chapter VI). In the case of the latter, some attention has been paid to the development of cotton types which would yield fibers showing improved papermaking qualities. Promising results have been obtained.

D. BAST FIBERS, FIBROVASCULAR ELEMENTS, CEREAL STRAWS, AND GRASSES[1,2]

SIDNEY D. WELLS

This section will deal primarily with the use of bast, stem, and leaf fibers for the preparation of cellulose pulps and not with the use of these fibers for textiles or cordage. Regardless of the end use of the fibers, the isolation of the fibrous constituents of the plant material from the nonfibrous constituents is largely mechanical. The filamentous character of the fibrous elements is retained as much as possible when use for spinning and weaving is contemplated, whereas reduction to the ultimate fiber, usually too short for textile purposes, is practiced when use for papermaking or chemical cellulose is the objective.

The bast fibers form fiber bundles between the outer bark and the woody portion of the stems of plants. Their function is to give strength and flexibility to the stem. Bast fibers are also called "soft" fibers. Before they can be used in the chemical cellulose, paper, or textile industries, they must be separated from the wood of the stem and to a greater or less extent from the gums and other materials which hold them together to form the inner bark. The ultimate fibers of which these bundles are composed are generally short, so that, except for chemical conversion, the bundles themselves are not broken down this far.

The fibrovascular elements of plants are the veins of the leaves and stems. Their function is not only to give rigidity, as is the case with the bast fibers, but also to transport water and plant foods. These vessels with their protective tissues form fibers that are larger and stiffer than the bast fibers. Hence, they are often known as "hard" fibers.

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[1] This section is in part a revision of that on "Bast Fibers" prepared by Kyle Ward, Jr., for the first edition, pp. 539–549.

[2] In Bibliography Series No. 176 of The Institute of Paper Chemistry, Part II by C. J. West, is given an annotated bibliography of bast fibers up to August, 1950; in Part I, Series No. 171, is given an annotated bibliography of cereal straws up to October, 1949. Additional information can be found in the Bibliography of Papermaking published by the Technical Association of the Pulp and Paper Industry. The availability of these bibliographies makes unnecessary the inclusion of many literature references in this contribution.

The cereal straws, cornstalks, sugar cane, and esparto are all derived from plants that are classified as grasses and are monocotyledons. Mechanical separation of the fibrovascular bundles is rarely practiced because of the futility of the operation; pulping is accomplished by digestion of the material as harvested without any effort to remove the nonfibrous constituents before cooking. Separation after pulping can be accomplished but usually paper or board made therefrom contains both the nonfibrous and the fibrous elements in much the same proportions that they occur in the original plant material as harvested.

1. Bast Fibers

The principal bast fibers are flax, hemp, jute, ramie, and paper mulberry. Other less important sources are sunn, kenaf, cadillo, baobab, nettle, hops, okra, milkweed, lespedeza, soybean, kudzo, sweet clover, and alfalfa.[3] Rarely can the value of the bast fiber, for papermaking or chemical cellulose, warrant the cost of cultivation and collection for those purposes alone. Although much work has been done in studying these fibers primarily for papermaking, the information gained has been of academic interest and the instances of verification through commercial use are exceedingly rare. When the flow of commerce is interrupted by war, interest in new fibers and sources of fiber becomes active, but when normal exchange of products in international commerce is restored, the well-established sources regain their pre-eminence. Much hand labor is usually required to produce an adequate supply of these substitute fibers for further processing for dissolving pulps, papermaking, textiles, and cordage. This can be accomplished only in those sections of the world where such labor is available at rates much lower than in more industrially advanced areas.

Bast fibers were the principal source of cellulose for papermaking for many centuries before the cotton fiber occurred in any important quantity as rags available for papermaking purposes. Linen, from the flax plant, was by far the main standby and it still excells in its adaptability for use in the highest grades of paper. When the flax plant is grown for fiber, the seed is sown more densely so that the plants crowd each other and the stems are comparatively free from branching until reaching the crown; the production of seed is a minor consideration. When raised for seed for linseed oil, as is largely the case in the United States and most flax-producing countries in the temperate zones of the world, the seed is sown more widely and the plant is more branchy in character. For many years the straw obtained as a by-product from the production of flaxseed has been burnt or allowed to rot in the fields to the extent of several million tons each year in the United States and in comparable amounts in Canada, Argentina, Russia and India, which are important areas in the production of flaxseed.

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[3] J. M. Mathews, *Textile Fibers*, 5th ed., Wiley, New York, 1947.

The actual plant fiber from which the bast fibers are derived usually amounts to from 10 to 20% by weight of the stalks or stems. The remainder is waste or, at best, a source of fuel to operate the necessary equipment. The decortication of flax straw exemplifies the processing and general principles involved in all bast fiber production. Mechanical treatments which remove the nonbast woody fragments of the stem from the fiber include the rippling or separation of the seed, decortication of the fiber, and scutching; these operations require considerable hand labor. Preliminary mild enzymatic treatments (called retting) decompose the pectins and gums and thus facilitate the mechanical separation without degradation of the cellulose. However, retting processes are, in general, too expensive for production of bast fiber for papermaking.

When rags or textile wastes are available at the price of rags or cuttings, it is uneconomical to start with the original flax plant for the manufacture of paper. Rags and cuttings have benefited by all the treatments through which the preparation of the textile product has proceeded.

The straw from seed flax, on treatment with brakes, is commercially useful as upholstery tow and insulation quilts. In the United States alone, however, several million tons of flax straw are produced in an average year and only an insignificant quantity is used for industrial purposes. The manufacture of cigaret paper from flax straw utilizes part of this agricultural residue which would otherwise be wasted. During the years leading up to the 1930's, the manufacture of cigaret paper occurred to the largest extent in France and other European countries. A few mills existed in the United States but not nearly enough to supply the domestic needs. Linen rags supplied the largest proportion of the fiber used. With the threatening conditions occurring in the late thirties, it became apparent that the supply of foreign cigaret paper or of imported linen rags would probably be seriously restricted. Consequently, the domestic manufacturers in the field studied the factors involved in producing cigaret paper from flax tow obtained from seed flax straw and to a remarkable extent were successful. The Forest Products Laboratory had been engaged during the 1920's in pulping flax tow with various cooking liquors.[4] Those composed of caustic soda and sulfur or caustic soda and sodium sulfide mixtures (similar to those used in kraft wood pulp practice) showed considerable promise when applied to flax tow. Multistage chlorination, caustic extraction, and mild hypochlorite bleaching had also been developed in the early 1930's, so that the tools became available to produce pulps from flax tow that made very satisfactory cigaret papers. The newest and largest mill in the field was built in North Carolina, making the United States self-sufficient in its total production of cigaret paper. In the United States 200,000 to 300,000 tons of flax straw were utilized annually for making cigaret paper in 1948 to 1951. The yields of bleached fiber amounted to approximately 8% of the weight of the original flax straw processed.

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[4] E. R. Schafer and C. E. Curran, U. S. Forest Products Laboratory, Mimeographed Report **R1159** (1938).

Flax pulp must produce paper having wearing properties impossible of attainment with cotton fiber or wood pulp to justify consideration. The needs for the great majority of paper products and dissolving pulps can be met by cotton or purified wood pulps. Under these circumstances it is very difficult, if not impossible, to organize the collection, transportation, and purification of agricultural residues on a substantially competitive basis.

Although the utilization of flax straw in the manufacture of cigaret paper has indicated a limited solution of the use of this agricultural by-product, there still remains 85 to 90% of the total annual production which finds no commercial use. In the manufacture of cigaret paper, a certain amount of degradation of the cellulose in processing can be permitted. If a large portion of the annual crop is to be used, the original degree of polymerization of the cellulose in the bast must be preserved. At the same time, a higher purity of the cellulose is necessary if utilization is to be extended to the manufacture of banknote or currency papers or if the fine paper manufacturers are to be induced to pay a price greater than the prevailing prices of high-grade cotton rags or purified wood pulps. The actual flax fiber that withstands all the various stages of pulping and purification and which, under the best conditions, occurs in the final paper product, amounts to about one ton per fifteen tons of flax straw harvested for the purpose. The value of the final product must justify the large volumes of raw material entering the system. Textile fibers have long been sold at prices that can justify such costs. Closer integration of the production of the so-called "line" fiber for textiles and cordage, with the utilization of the combings as tow for papermaking, may be possible and, to whatever extent it is, the economics of the system can be benefited. The demand for textile fiber must be balanced by the demand for papermaking fiber. When not in proper balance, the benefits of integration may cease to exist.

Hemp for textile purposes undergoes a type of retting process similar to that employed for flax. The fiber thus obtained is used in ropes and cordage and as a substitute for flax in the cheaper linens. Hemp is grown widely in Europe and Asia, and, to a lesser extent, in the United States. In the last country its growth is controlled by law, since the narcotic marijuana is produced from the same plant.

Jute is also retted, usually in pools of stagnant water. When retting is complete (from 10 to 20 days), the bast fiber is easily separated from the woody stem. As a textile it is used in twines and cordage and in rough fabrics, such as carpet backing or burlap bags.[5] India produces practically the entire world supply of jute.

Ramie finds much less commercial utilization than flax, hemp, and jute fibers. The reason for this lies, in part at least, in the difficulty of purifying and spinning the fiber. Simple retting is not sufficient for removing the bast fiber, as in the case of the preceding crops, and none of the many mechanical methods suggested for decortication has established itself industrially. In China, the bast fibers are stripped off by hand in long ribbons. The bark and some of the gums are scraped off, also by hand. The fiber thus obtained must be further degummed before spinning, which is difficult to do without injury to the fiber. Retting is not satisfactory, and chemical treatments, especially alkaline cooks, seem to be the most promising. Ramie is grown in quantity only in the Far East,[6] although small plantings,[7] mostly for experimental purposes, have been made at many places in the southern part of the United States.

The bast fiber of the paper mulberry is unusual in that the fiber is processed into a fabric without either spinning or weaving. The clean fibers are laid out wet in several layers and allowed to dry overnight. The next morning they will be found to have adhered to each other to form a single layer which is beaten with a wooden mallet until it forms a smooth strong cloth.[3] The paper mulberry is grown in India and Japan and on the islands of the Pacific.

Sunn is prepared by a retting process similar to that used for true hemp and finds its main use in the preparation of nets and cordage. This plant is grown extensively in Southern Asia.

Kenaf is used like jute for cordage and sacking but, in general, is inferior. Cultivation and processing are also similar to that of jute. Kenaf is said to have been introduced into India from Africa. Today the commercial crop is almost entirely obtained from India, and one frequently used name for the fiber is Deccan hemp, the name coming from the section of India in which kenaf is grown. Gambo hemp and ambari hemp are other names for the same material.

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[5] N. C. Chaudhury, *Jute and Substitutes*, 3d ed., W. Newman & Co., Calcutta, 1933, 249 pp.

[6] G. L. Carter and P. M. Horton, *Ramie*, Louisiana State Univ. Studies No. **26**, L. S. U. Press, Baton Rouge, 1936, 100 pp.

[7] L. H. Dewey, U. S. Dept. Agr., *Misc. Pub.* **518** (1943), 95 pp.

Cadillo or urena fiber[6] is the bast fiber from certain tropical shrubs which include *Urena lobata* and *Urena sinuata*. These fibers, with those from some other shrubs, are now being designated as Cuban jute and are recommended as substitutes for true jute.

The bast fiber of the baobab, or monkey's bread tree (*Adansonia digitata*), is known as Adansonia fiber and finds some use as cordage. The tree is a native of Africa, but is now grown in both the East and the West Indies.

The nettle is reported to be an excellent textile fiber and received a great deal of attention in Germany during the war years of 1914–18 and 1939–45. The fiber content of the wild nettle is about 6%, but this has been increased by cultivation to 12–13%. The fiber may be separated from the stalk by retting, as with flax, or by mechanical decortication, as with ramie. In either case, strips of fiber are obtained which must be chemically degummed.

The hop fiber can be separated by retting, but the process is time consuming and not very practicable.

The bast fiber of the potato plant has been studied in Germany for textile purposes, but it does not appear to be economically practical under normal circumstances.

The bast fibers of certain trees, such as the willow or sequoia, have found some very limited applications in textiles, usually as cordage or felting materials. The bast of the castor bean plant has also been recommended for this purpose.

2. Cellulose Pulps from Bast Fibers

The bast fibers have never had any industrial importance in the preparation of rayon or of chemical cellulose except when increased demand and interruption in the supply of cotton and wood pulp may have caused a search for other sources. There is considerable patent literature on the subject.[2] The following is a brief summary of the methods proposed for the utilization of these materials.

There are three possibilities to be evaluated if any bast fiber plant is to be considered as a source of cellulose. First, the separated bast fiber may be used. However, the quality of these long fibers is very high, and they are usually too valuable for textile purposes to compete with cotton or chemical wood pulp in the cellulose industry, except in the form of rags or similar textile wastes. Second, the woody residues from the bast fiber separation may be pulped. These residues have received considerable attention in the case of the important textile materials, flax and hemp. Third, the entire stem may be treated. This is not simple, for a process capable of completely pulping the woody portion is so drastic that the bast fibers lose the ability to resist wear for which the bast plant was chosen. Cotton rags or wood pulp can usually be obtained in a free market at a cost lower than that of collecting and processing fibrous plants; if the special properties possessed by the bast cellulose are lost in the processing, there is no point in trying to utilize them. Flax straw is decorticated by breaking between rolls to "fine tow" amounting to about 20% of the original straw. It is then cooked with approximately 15% caustic soda and 5% sodium sulfide. The ultimate yield of paper is one ton from fifteen tons of straw. Flax straw is now the source of much of the fiber in the long-established mills engaged in the manufacture of cigaret paper in western Massachusetts, New Jersey, and Pennsylvania and in a new plant in North Carolina. When the decorticated fiber is used for papermaking, the mechanical treatment may be carried to the extent that the tow is too short for the purposes other than paper or chemical cellulose manufacture. More complete removal of the nonbast constituents is possible, however, without degrading the cellulose of the bast, as is invariably the case when chemical methods are used. It has recently been found possible to produce bleached pulps of high viscosity satisfactory for the manufacture of banknote paper and for use with cotton in the manufacture of high-grade ledger and other rag papers. The mechanical disintegration of the woody matter, when about 95% dry, proceeds much faster than that of the bast fiber when the tow or fluff is beaten with rods; the bast fibers can be isolated by means of screens and by pneumatic separation, and are then treated at room temperature with dilute caustic soda. Finally, with multistage chlorination, caustic extraction, and bleaching, a shive-free pure white pulp is secured having a TAPPI viscosity greater than 100 centipoises.[8]

Where the special wearing characteristics of the bast fibers are desired, primarily because cotton and wood pulp fibers are incapable of such development, it is obvious that the woody shive from the flax stem or branch structures must be removed as completely as possible before any chemical pulping occurs. Otherwise, the cellulose fibers and cells from the pulping of the shive will contaminate the bleached bast pulp and the paper made therefrom will appear, on microscopic examination, to be adulterated with wood pulp. With complete decortication of the straw, the yield of bast should not exceed 20% of the original chaff-free straw. On subsequent pulping and bleaching, the final products, free from cellulose derived from the shive but containing all the bast, cannot exceed 12.5% of the original agricultural residue. It is consequently apparent that only manufacturers of the papers that command exceedingly high prices can afford to use it. The properties possessed by the properly prepared fiber, however, are such that the high cost is justified.[9, 10]

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[8] S. D. Wells (to The Institute of Paper Chemistry), U. S. Patent 2,298,994 (Oct. 13, 1942); *Chem. Abstracts*, **37**, 1868 (1943); U. S. Patent 2,452,533 (Oct. 26, 1948); *Chem. Abstracts*, **43**, 3198 (1949); and patent applied for.

3. Fibrovascular Elements

Many fibers used in commerce and industry consist of filaments of indefinite length rather than individual fibers. These filaments are obtained by separating the fibrovascular elements of stems and leaves from the parenchyma tissue by means of scraping, beating, scutching, and combing, usually by hand. The product is valued principally for its strength, either wet or dry, and its ability to be spun or twisted into cords or coarse threads which can be used for rope, cordage, or twine and in coarse textiles, such as burlap, bagging, netting, matting, and hammocks. The filaments have essentially the same chemical composition as the original plant, and the presence of noncellulosic matter is not important in so far as it does not affect the durability, strength, or other physical properties of the product made therefrom. Their value for cordage is usually so much more than the prevailing price of paper stock that they are usually not considered as sources of cellulose. Among the fibers of this class may be mentioned the following: henequen, sisal, abacá, phormium, and caroa. In addition are latona, mescal, zapupe, cantala, ixtle, pita, cabuya, fique, cocuiza, pitre, yucca, banana, palm, palmetto, zray, and toquilla which have local importance or which enter occasionally into world commerce. They are all generally classified as leaf fibers and comprise from 10 to 20% of the leaf and stem substance from which they are derived.[7]

When these materials are subjected to the usual alkaline cooking treatments, the individual ultimate fibers are liberated and the noncellulosic constituents are dissolved. The lengths of the ultimate fibers bear no relation to the lengths of the filaments from which they were derived. Sisal, for instance, yields a fiber not much longer than short-fibered hardwoods,

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[9] H. S. Spencer, *Pulp & Paper Mag. Can.*, **47**, No. 10, 95 (Sept., 1946).

[10] G. H. Lafontaine, *Pulp & Paper Mag. Can.*, **52**, No. 7, 142 (June, 1951).

uch as poplar, beech, birch, or maple. Manila hemp and caroa, on the ther hand, yield a very long and uniform fiber, capable of use in the manuacture of high-priced papers suitable for special uses such as tags, sandaper, flour sacks, electric insulation, tea bags, stencils for mimeographing, nd lens paper. These fibers do not fibrillate or hydrate on beating to the ame extent that bast fibers, wood pulp, or rag fibers do, and papers made herefrom are characterized by an unusual combination of porosity, resistnce to wear, and wet and dry strength (see Chapter VIII).

4. Cereal Straws

Rye, wheat, oat, and barley straws have been an important source for ellulose fiber since the invention of paper between A.D. 25 and A.D. 58 by sai L'un, secretary in the court of Honaug-Han, emperor of China. In act, the use of straw antedates linen and cotton rags as well as wood pulp, he most important source of cellulose at the present time. At the time of nd prior to about 1860, straw was the principal source for cheaper papers, nd most of the newspapers of that period were manufactured from a mixure of rag and soda straw pulp. Newspaper files of the Civil War period n our large public libraries are in much better condition than those of the irst World War because of the greater permanency of straw pulp as comared with groundwood pulp.

With the advent, during the last half of the last century, of the soda, ulfite, and sulfate processes for pulping wood (in addition to the mechanial process which was invented in 1855) (see Section A of this Chapter VI), traw was replaced by wood pulp on account of the lower cost of producing he latter, and straw pulp is now used only in papers where it is desired to npart properties such as most even formation not possessed by papers ade from the more recent competitors. Advances in the art of pulping, owever, have greatly enlarged the possibility of reducing the cost of pulps rom cereal straws. Some of the more recent processes, such as multistage leaching with chlorination and caustic extraction, have so improved the uality and so enlarged the range of properties which can be obtained that seems probable that the use of straw may attain a relatively more imortant role in the future. In the older and longer established industrial ountries, straw has always retained its position as a source of cellulose. seems reasonable to expect that this position will be regained to an imortant extent in the United States as the supply of virgin timber becomes ore limited and the dependence upon second or third growth cordwood ecomes more common.

Most of the straw used for paper pulp in the United States is cooked with milk of lime, dolomite lime being preferred. About 10% of calcium oxide or 13% of burnt dolomite is required. The cooking is carried out in spherical rotary digesters at a temperature of about 115°C. for 8 to 10 hrs. There is usually considerable false pressure, so that the pressure as shown by the pressure gage will usually be at least 45 lb./sq. in. After cooking, the pressure is relieved (this is accompanied by the escape of considerable ammonia produced during the digestion), and the contents are dumped on a conveyor and piled in heaps for drainage and a further softening of the knots and more resistant portions through seasoning in the presence of the spent liquors. The material is then washed in beaters equipped with drum washers, or the spent liquor is pressed out by means of screw or roll presses, and the fibers separated by passage through rod mills. The product may be further washed on vacuum filters or decker washers and is then suitable for further treatment with jordans for the manufacture of corrugated paper, capstock, egg-case filler board, and ordinary stiff cardboard.

The yield of board obtained is usually between 65 and 70% of the weight of straw used; the mineral matter present varies from 10 to 15%, of which about half is silica and the other half magnesium and/or calcium compounds.

When the straw is reasonably free from weeds and has been baled while dry and stored under cover, the pulp obtained as described above can be bleached with chlorine, caustic extraction, and hypochlorite in several stages to produce a superior white pulp which is suitable for high-grade uses. Only since 1932 has availability of suitable equipment made this procedure possible and then only in locations where stream pollution from the spent cooking liquors is not objectionable. Ultimate yields up to 50% of the weight in the dry straw are obtained; this fiber is softer and not so easily slowed down in draining properties as when the older conventional cooking methods are used.

Among the foremost common cereal straws, rye straw is preferred because of its somewhat longer fiber and higher cellulose content; wheat straw comes next. Oat straw is used where the supply of the other two is inadequate; the yield of cellulose obtained therefrom is noticeably lower, and the pulps produce a paper or board inferior in strength. Barley straw is objectionable on account of the beards which are not readily reduced in the cooking operation.

The soda and sulfate processes are well established in continental Europe and for the last decade have been used in Great Britain. The silica present in the straw interferes with settling in the causticization of the recovered soda, so that recoveries of 65 to 80% are more common as compared with 80 to 90% for soda and kraft pulp mill processes in which wood is used.

In recent years, several pulp and paper mills have been built in South America, South Africa, Europe, and the Phillipines which use the Pomilio process[11] for the pulping of cereal straw and bagasse. The process consists of digestion of vegetable fibrous material with caustic soda at moderate temperature and concentration, washing, treatment with chlorine, extraction with dilute caustic soda solution, washing, and bleaching with calcium hypochlorite. It differs from the multistage bleaching of mildly cooked soda pulps in that a much greater part of the pulping and purification of the plant material is accomplished by the chlorine than by the caustic soda. The electrolytic production of chlorine and caustic soda is an important part of the process, and sodium chloride is considered the primary chemical rather than caustic soda or chlorine.

World patent rights to the Pomilio continuous process have been acquired by the Cellulose Development Corporation of Hatch End, Middlesex, England. With the experience gained by the operation of a pilot plant of a daily capacity of about three tons, this firm has designed and built over twenty commercial plants in various parts of the world, among which is the Cie Nord-Africaine de Cellulose recently built and placed in operation at Baba-Ali in Algiers. The process used in these plants is completely continuous and is known under the name of Celdecor-Pomilio. Straw and esparto grass are the only fibrous raw materials processed in the ast-named plant, and production is reported as 35 tons of high-grade white paper per day.

Caustic soda will pulp wheat and rye straw[12] if the chopped material, in he presence of five to six times its weight of water, is passed through two rod mills in series at temperatures between 95 and 98°C. The pulped material can be further purified by digestion under 60-lb. pressure in rotary cookers with an excess of caustic soda. The partially spent cooking liquors can be used as the source of caustic soda in the preliminary treatment with ods, so that a two-stage cooking system results with countercurrent flow of the cooking chemical. Unusually effective utilization of the chemical is hus attained, with higher yields and more effective use of equipment because of the reduction in bulk of the straw through the rod mill action.

Cereal straw may be pulped effectively by means of sodium carbonate nd sulfur or sodium sulfite. Both processes have been adopted by American strawboard manufacturers in the production of superior corrugated paper under the name of "Strawkraft" and odorless egg-case fillers under

[11] T. G. L. Becker, "Twenty-five Years' Pulping Developments of Agricultural Residues," *Paper Trade J.*, **132**, 16 (Mar. 23, 1951).

[12] S. D. Wells and P. A. Forni, *Paper Trade J.*, **112**, 32 (June 12, 1941).

the name of "Nuprocess." Yields of 65 to 70% of fiber are realized, and products are obtained which are from 50 to 100% stronger than corresponding products cooked with lime. The extension of the use of Hydrapulpers, Dyno Pulpers, Pulpmasters, and similar equipment to straw pulping has recently shown considerable merit when active reagents such as caustic soda and sodium sulfide are used. The Northern Regional Laboratory has designated the process as the mechanicochemical process.[13] Recent developments have shown that superior pulps can be made from cereal straws by using dilute caustic for soaking the straw from 48 hours to 3 days at room temperature.[14] The Cartiera F. A. Marsoni at Villorba in Italy has used for several years a cold caustic process in the production of very satisfactory greaseproof and glassine papers from cereal straw.

5. Esparto Grass

Esparto was first used as a source of papermaking cellulose fiber by Thomas Routledge in Great Britain in 1856. It has since become one of the major sources for fiber in Great Britain and is imported from Spain and Northern Africa. Bales of the grass are used as return cargo in steamers transporting British coal to countries bordering the Mediterranean.

The bales of grass on receipt at the paper mill are opened, dusted in a conical duster or willow, and charged into a vertical digester larger in diameter in proportion to height than is customary in cooking wood by either the soda or kraft processes. The digester is provided with a perforated false bottom through which the cooking liquor is withdrawn and pumped to above an annular perforated distributing plate just below the top of the digester. This plate distributes the liquor uniformly over the charge. In the course of 2.5 to 3 hrs. the digestion is completed. In filling a digester, several additions of the loose grass are necessary to make a complete charge (in much the same manner as when straw is charged into the globe rotaries used in American strawboard mills) since the material packs more closely as cooking proceeds. Rotaries are not used, however, because of the objectionable effect of the rotation on the fiber structure. Vessels holding as much as seven tons of esparto grass have been reported in use. The liquor charged will test 45 grams per liter of NaOH and the temperature used may reach 148°C. with a gage pressure of 50 lb./sq. in. On completion of the cook, the steam is blown off to recover the heat, and the strong black liquor is allowed to drain. The charge of chemical and the volume of liquor may be changed to meet variations in the quality and condition of the grass; these modifications are a matter which depends upon the judgment of the supervisors. A more extensive description is given by Beveridge.[15]

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[13] S. I. Aronovsky in J. Newell Stephenson, editor, *Pulp and Paper Manufacture*, Vol. 2, McGraw-Hill, New York, 1951, pp. 67–69, 76, 77.

[14] S. D. Wells (to Mine & Smelter Supply Co.), U. S. Patent 1,769,811 (July 1, 1930); *Chem. Abstracts*, **24**, 4634 (1930).

After the strong black liquor is drained off, the pulp is flushed with hot washings from earlier cooks and finally with hot water. The pulp is then treated in much the same manner as that followed in wash pan or diffuser operation in soda and sulfate mills operating on wood.

Papers made with esparto pulps as the major portion of the furnish have excellent bulking properties. The faithfulness with which they reproduce the tones and impressions of type and plates accounts for the distinctiveness of printing in England. Although the length of the fibers is less than that obtained from coniferous woods, the fiber diameter is much less and the strength of the paper obtained is ample for printing purposes. The retention of china clay, with which Great Britain is abundantly supplied, is unexcelled and the over-all cost of the furnish compares favorably with the cost of furnishes based upon wood pulps made by the sulfite and soda processes.

Furnishes containing esparto pulps in considerable proportion remain dispersed to a remarkable degree in the formation of the web on the wire of the paper machine and resist agglomeration better than most other fibers. For this reason the formation of the sheet is usually better. There is probably a close relationship between this property and the retention of clay with which the use of esparto is usually associated.

Considerable success is also reported by users of the Celdecor-Pomilio process in pulping a wide range of fibrous agricultural residues and fibrous materials derived from the grasses, and the organization of harvesting techniques and machinery can be expected to follow the more extended use of such materials.

6. Bamboo

Bamboo is now an important source of cellulose in India. The soda process as modified by Raitt[16] is used; it involves the preliminary crushing of the bamboo nodes and countercurrent use of the alkali in a two-stage digestion. Higher yields of cellulose are obtained than from cereal straws, but the operation must bear the cost of the collection, whereas with cereal straw this cost is borne by the grain. In India, where the supply of bamboo is enormous and labor exceedingly cheap, an industry of considerable magnitude has become established.

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[15] J. Beveridge in J. Newell Stephenson, editor, *Pulp and Paper Manufacture*, Vol. 2, McGraw-Hill, New York, 1951, pp. 85–91.

[16] W. Raitt, *The Digestion of Grasses and Bamboo for Papermaking*, Crosby, Lockwood & Son, London, 1931, 116 pp.

7. Bagasse and Cornstalks

Bagasse and cornstalks have been the subject of papermaking developments on numerous occasions since the middle of the last century. These efforts have all failed because of the bulkiness of the raw material, the large proportion of nonfibrous cellulose which is less resistant to pulping than the fibrous material, and the fact that most attempts to utilize new materials are in the hands of promoters rather than under the guidance of established operators. For the future, however, with advances in pulping technology, it is conceivable that bagasse pulping operations can be made feasible where the economics of competitive materials will allow it.[17] The procedure referred to for use on wheat straw, which consists of a countercurrent two-stage cook with the rod mill as a continuous digester for the first stage, has been found to be particularly applicable to bagasse and cornstalks. The nonfibrous cellulose material produced is used as a stiffening agent in paperboard manufacture, and bleached cellulose fiber is used for light-weight and high-grade papers for numerous uses. Four tons of cornstalks or bagasse have been found to yield one ton of high-grade bleached cellulose fiber and one ton of the nonfibrous material mentioned above.[18]

8. Value of Annual Plants

In the manufacture of viscose rayon and staple fiber, purified straw pulp found use in Germany in the 1930's. For cellulose esters, such as the nitrate and acetate, and cellulose ethers, such as the methyl and ethyl ethers, cotton linters, and purified wood cellulose low in pentosan content are preferred. The pulps obtained from annual plants, especially cereal straws which comprise the largest source of cellulosic material collected as a step for the harvesting of a more valuable product, have a high pentosan content; where this constituent is unobjectionable, an enormous source of material is available.

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[17] *Chem. Eng. News*, **30**, 2708 (1952).

[18] S. D. Wells and J. E. Atchison, *Paper Trade J.*, **112**, 34 (Mar. 27, 1941); S. D. Wells, U. S. Patent 2,029,973 (Feb. 4, 1936); *Chem. Abstracts*, **30**, 2000 (1936); U. S. Patent 2,181,556 (Nov. 28, 1939); *Chem. Abstracts*, **34**, 2174 (1940); *Ind. Eng. Chem.*, **21**, 275 (1929); S. D. Wells and R. Steller, *Paper Trade J.*, **116**, 45 (Apr. 15, 1943).

The degree to which plant fibers can be used in paper manufacture depends upon the dimensions of the fibers, the proportion of fibrous to nonfibrous cells, and the physical properties of the fiber, rather than upon the chemical properties of the pulp. With the exception of the bast fibers of flax, hemp, ramie, and the like, the pulps from annual plants are high in pentosans and hemicelluloses. The fibers "hydrate," that is, become more resistant to drainage of water, on mechanical treatment more easily than wood pulps or rag fibers; in general, this property limits their use to papers in which the amount of mechanical treatment given the pulps is comparatively mild. The retardation of free drainage on mechanical treatment (in some instances even pumping) interferes with the subsequent bleaching and washing operations, with the formation and drainage of the sheet on the fourdrinier wire or cylinder mold, and with the removal of the water from the sheet on the presses. Consequently, weak brittle paper often results, or the rate of production of the paper may be retarded. With due consideration of these properties, however, annual plant fibers may contribute to the quality of the product or reduce the cost of fabrication. They are not suitable, however, as general-purpose pulps and should be used only in papers where they contribute definitely desired characteristics.

Cereal straws have been used as a source of cellulose fiber for paper and other products throughout the Christian era. The feasibility of their use depends entirely upon economic factors. Recent improvements in pulp purification will probably extend the use of straw, particularly for paper products to which its fiber will impart the superior sheet-forming properties. The same may be said of grasses such as bamboo, bagasse, and cornstalks. Utilization of the nonfibrous cells as a stiffening agent in ordinary paperboard further contributes to the feasibility of the use of annual plants as a source of cellulose fiber. Of the agricultural fibrous residues occurring each year, probably cornstalks comprise the largest single item in the United States; the annual volume amounts to probably over 40 million tons. Much study has been applied to the utilization of cornstalks, and several industrial ventures have been attempted. The perfection of systems of good roads in the corn belt has greatly contributed to the feasibility of utilization. The possibility of employment during the winter months is always attractive except during war periods when labor is unusually scarce. The storage of cornstalks has been found to be feasible through periods of several years duration at Ames and Dubuque, Iowa, and Danville, Illinois; the losses have been no more and to some extent less than in the storage of baled straw. All that seems necessary for solving the problem of utilizing cornstalks is the assurance of a dependable outlet to justify the attention of agricultural engineers and manufacturers of farm equipment. With the integration of paper and board manufacture, the assurance of a supply of baled shredded cornstalks, and an outlet when the supply is assured, there seems to be no valid reason why much of this fibrous residue annually occurring cannot be profitably utilized.

CHAPTER VII

BLEACHING AND PURIFICATION OF WOOD CELLULOSE

R. S. HATCH

The bleaching of wood cellulose, from one point of view, represents a continuation of the pulping process. The objective of pulping is the removal of the maximum amount of noncellulosic constituents in wood (lignins, fats, waxes, tannins, water-extractable material, and carbohydrates related to cellulose in nature) through the use of relatively low-priced chemical reagents, with a maximum yield of crude cellulose. Attempts to remove all the noncellulosic material by such methods result in severe degradation of the cellulose itself and subsequent loss of yield. The bleaching processes applied to this crude wood cellulose effect further purification under relatively mild, controllable conditions. A more obvious function of bleaching, as the name implies, is the actual whitening of the pulp. In some instances, this is simply a manifestation of the particular state of purity achieved. In other cases, the whitening action involves destruction of colored contaminants without appreciably raising the degree of refinement.

A. GENERAL PRINCIPLES

The techniques employed in bleaching of wood cellulose are dependent on the nature of the pulp being processed and on the anticipated end use.[1] Processing details fall into one of three general categories in accordance with the following objectives:

1. For certain types of pulp such as groundwood or semichemical pulps, the objective is the partial removal, or alteration, of the colored noncellulosic residues to provide a product of satisfactory brightness or "whiteness"

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[1] For an excellent discussion of the bleaching of pulps, see also J. P. Casey, *Pulp and Paper*, Vol. I, Interscience, New York-London, 1952, Chapter V; F. Kraft in J. N. Stephenson, editor, *Preparation & Treatment of Wood Pulp* (Pulp & Paper Manufacture, Vol. I), McGraw-Hill, New York, 1950, Chapter 7.

to serve as a background for printing and illustrations, without materially reducing the yield of these pulps with respect to the original wood.

2. The bleaching of chemical pulps, commonly designated as sulfite, sulfate, and soda pulps involves substantially complete removal of noncellulosic impurities as well as the production of a finished product having a satisfactory degree of brightness. The extent of brightness desired is dependent on end use.

3. Pulps intended for the manufacture of cellulose derivatives are further purified during the bleaching operations through the removal of carbohydrates (such as pentosans, hexosans, and uronic acids) which normally accompany the pure cellulose as it exists in wood.

It is possible by specific oxidation or reduction treatments to bleach the colored noncellulosic contaminants (chiefly lignin) in a crude wood cellulose furnish. Such techniques are ordinarily applied to groundwood or semichemical pulps (process category 1). The removal of lignin can be accomplished by more severe oxidative methods which result in profound degradation of the aromatic system. At the same time there occurs considerable oxidative damage to other noncellulosics and to cellulose itself. A more selective and less expensive method for removing the bulk of the lignin is by means of chlorination, following which the chlorinated lignin can be washed out by appropriate methods. Further purification and simultaneous whitening of the pulp is normally effected by controlled oxidative treatments. Alkaline extraction processes are also applied if a further reduction in the level of noncellulosic carbohydrates is desired. The process involving chlorination and mild oxidative bleaching with or without alkaline extraction is customarily applied to the so-called chemical pulps (process category 2). The thorough refining of chemical pulp for cellulose derivative applications involves the use of more drastic alkaline extractions and preferably multistage oxidative bleaches (process category 3).

B. SPECIFIC BLEACHING TREATMENT

1. Chlorination

The first chemical wood pulp prepared in this country was made by the soda process which was brought here from England by Watt and Burgess in 1854. These pioneers proposed to use chlorination in the bleaching of soda pulp and obtained a patent[2] for a bleaching process, the first step of which was chlorination. The process was not a commercial success because

[2] C. Watt and H. Burgess, U. S. Patent 11,343 (July 18, 1854).

of the high cost of elemental chlorine at that time and because of the lack of suitable acid-resisting equipment for commercial operation. The use of elemental chlorine as a step in the bleaching process was not considered again until the end of World War I when liquefied chlorine became a cheap and readily available article of commerce.

For the bleaching of sulfate pulp in which chlorination was the first step, de Vains[3] obtained a German patent in 1913 and a U. S. patent in 1914. The de Vains patent was followed by a patent to Drewsen[4] in 1918 in which a very similar process was used. Cataldi[5] was granted a patent in 1916 for the use of chlorination in the bleaching of straw and other lignin-containing pulps.

In considering the action of chlorine on crude wood cellulose, there will be frequent occasions to use the term "bleachability." This represents a measure of the amount of chlorine in the form of an oxidizing agent which a given sulfite pulp will consume under certain standard conditions. Many different methods have been suggested for this purpose, but the one most used in this country is the TAPPI permanganate test.[6] The test measures the number of milliliters of 0.1 N $KMnO_4$ consumed in acid solution by one oven-dry gram of pulp under standard conditions of concentration, time, and temperature. Multiplication of this value by $0.355/x$ gives the so-called "chlorine bleachability," which is a rough approximation of the chlorine in the form of hypochlorite which would be consumed by 100 grams of pulp when bleached to a standard brightness.[7] The factor x varies with permanganate number between about 0.8 and 0.5 for the usual sulfite pulps. The method has been extended to sulfate pulps for which the factor x is generally 0.9 or higher. A recent article by Ålander[8] illustrates concisely the relationships between the various bleachability numbers.

When chlorine is dissolved in water, the following equilibrium exists:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \qquad (1)$$

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[3] A. R. de Vains and J. F. T. Peterson, German Patent 283,006 (Feb. 26, 1913); A. R. de Vains, U. S. Patent 1,106,994 (Aug. 11, 1914).

[4] V. Drewsen (to West Virginia Pulp & Paper Co.), U. S. Patent 1,283,113 (Oct. 29, 1918); *Chem. Abstracts*, **13**, 187 (1919).

[5] B. Cataldi, Brit. Patent 101,475 (Sept. 11, 1916); *Chem. Abstracts*, **11**, 209 (1917); French Patent 482,222 (1916).

[6] Tech. Assoc. Pulp Paper Ind., *Standards*, **T 214 m-50**.

[7] The term brightness is a measure of the light reflected from the surface of a sheet of pulp at a wavelength of approximately 457 millimicrons. This reflectance is measured with a spectrophotometer and is referred to the reflectance at the same wavelength of a surface of pure magnesium oxide (see Chapter XII-A-3-f).

[8] P. Ålander, *Finnish Paper Timber J.*, **33**, No. 6, 201 (1951).

It is obvious that the composition of this equilibrium mixture, and therefore its effect on organic matter, is highly dependent on pH. Thus, under very acidic conditions, pH of 2 or less, the solution contains chiefly dissolved undissociated chlorine. Although some oxidation can occur under these conditions because of the presence of some hypochlorous acid, the environment is conducive to chlorination as can be expressed by the equation (R designates the organic residue):

$$RH + Cl_2 \longrightarrow RCl + HCl \qquad (2)$$

As the acidity of the chlorine-water system is decreased, the formation of hypochlorous acid is favored with resultant increase in the rate of oxidative attack as represented below:

$$RH + Cl_2 + H_2O \longrightarrow ROH + 2HCl \qquad (3)$$

$$RCH_3 + 3Cl_2 + 2H_2O \longrightarrow RCOOH + 6HCl \qquad (4)$$

Increasing dissociation of hypochlorous acid to hypochlorite ion follows at higher pHs (above 5), and the rate of oxidation is thereby decreased since the latter has a somewhat lower oxidation potential than does HOCl. In alkaline environments, the reaction is slow but entirely oxidative.

Although there may be a brief preliminary oxidative attack of aqueous chlorine on cellulose and noncellulosic materials in a typical chlorination process (equations 3 and 4), the pH of the slurry quickly drops because of the hydrochloric acid liberated, and substitution of lignin hydrogens by chlorine (equation 2) then becomes the predominant reaction. It should be observed that the chlorination reaction maintains a high level of acidity because of simultaneous hydrochloric acid formation. When the lignin in the wood pulp is saturated with chlorine, a slow oxidation reaction then proceeds until all the chlorine is consumed. According to equation 2, one-half of the chlorine added should appear as hydrochloric acid when true chlorination is complete, but in the case of equations 3 and 4 all the chlorine added will appear as hydrochloric acid.

The course of a chlorination is illustrated by the curve in Figure 1. A sample of unbleached sulfite pulp having a test bleachability of 4.9% chlorine was suspended in water and thoroughly agitated. Chlorine gas was bubbled in at a fixed rate and samples were withdrawn at the points indicated on the curve. The ordinates on this plot represent the test bleachability after washing the samples withdrawn; the abscissas show the percentage of the chlorine consumed, based on the original test bleachability. This curve is a straight line to a point representing 30% of the test bleachability after which the slope begins to change, and at point A, which represents 40% of the test bleachability, the slope changes sharply and the curve again assumes a straightline character. Thus it would appear that true chlorination or substitution is dominant approximately as far as point A on the curve but from this point on oxidation as shown in equations 3 and 4 dominates. The ratio of hydrochloric acid formed to chlorine added will vary somewhat depending on how long the process is allowed to continue after point A is reached. In any case, at or shortly after the end of chlorination one would expect on the basis of stoichiometry that the ratio would be nearer to 1:2 than to 1:1. As confirmation of this view regarding the nature of the process, a number of investigators[9]–[12]

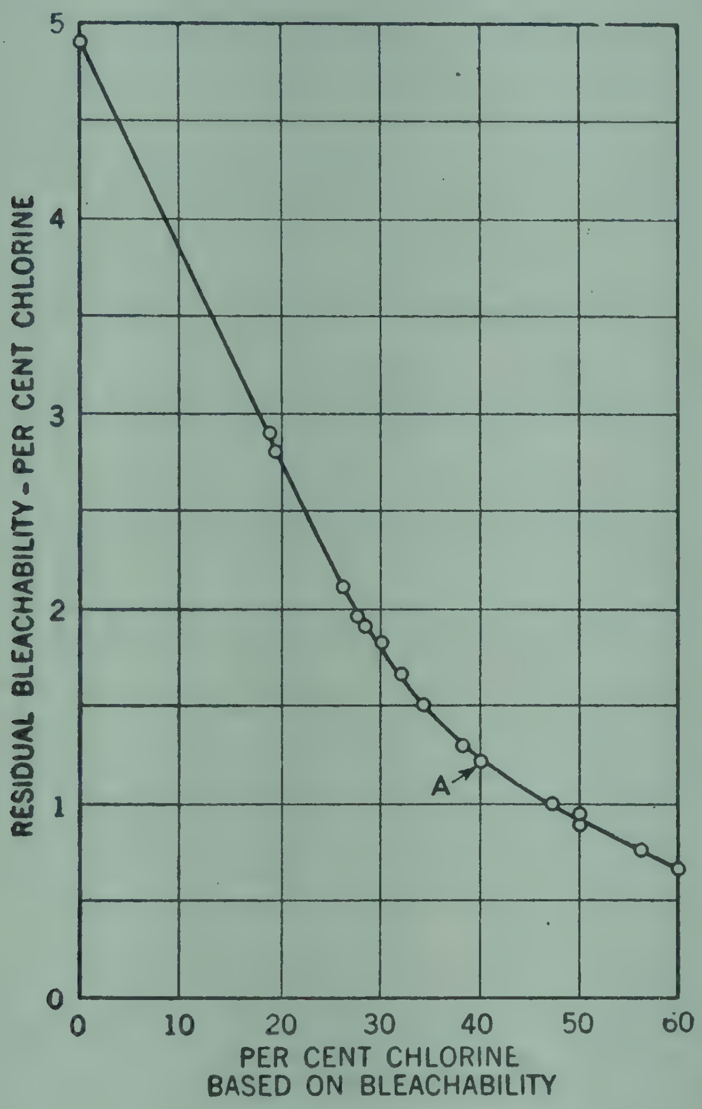

Fig. 1. Residual bleachability of a sulfite pulp versus the chlorine requirements for single-stage bleaching. True chlorination reaction is approximately complete at point A. From this point on, oxidation begins to dominate.

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[9] E. Heuser and R. Sieber, *Z. angew. Chem.*, **26**, 801 (1913).

[10] P. Waentig, *Papier-Fabr.*, **25**, Tech.-wiss. Tl., 340 (1927).

[11] L. Rys, *Papier-Fabr.*, **26**, Tech.-wiss. Tl., 256 (1928).

[12] O. Kress and E. H. Voigtman, *Paper Trade J.*, **97**, 29 (Aug. 17, 1933).

have found that between 50 and 60% of the chlorine added finally appears as hydrochloric acid.

The actual practice of pulp chlorination is illustrated by the following account which specifically concerns sulfite pulp. Experiments have shown that if a sulfite pulp is chlorinated to point A in Figure 1, and then the products of chlorination are washed out and the washed pulp is bleached with hypochlorite, the minimum amount of total chlorine will be required to bleach the pulp to a standard brightness. With sulfite pulp it is customary, however, to chlorinate to approximately 65% of the test bleachability and wash before the final bleach. This practice is followed because any additional degradation which may be involved in chlorinating to 65% rather than to 40% of the test bleachability is relatively small, and the overall cost of bleaching is less because chlorine in the form of hypochlorite costs about 50% more than elemental chlorine.

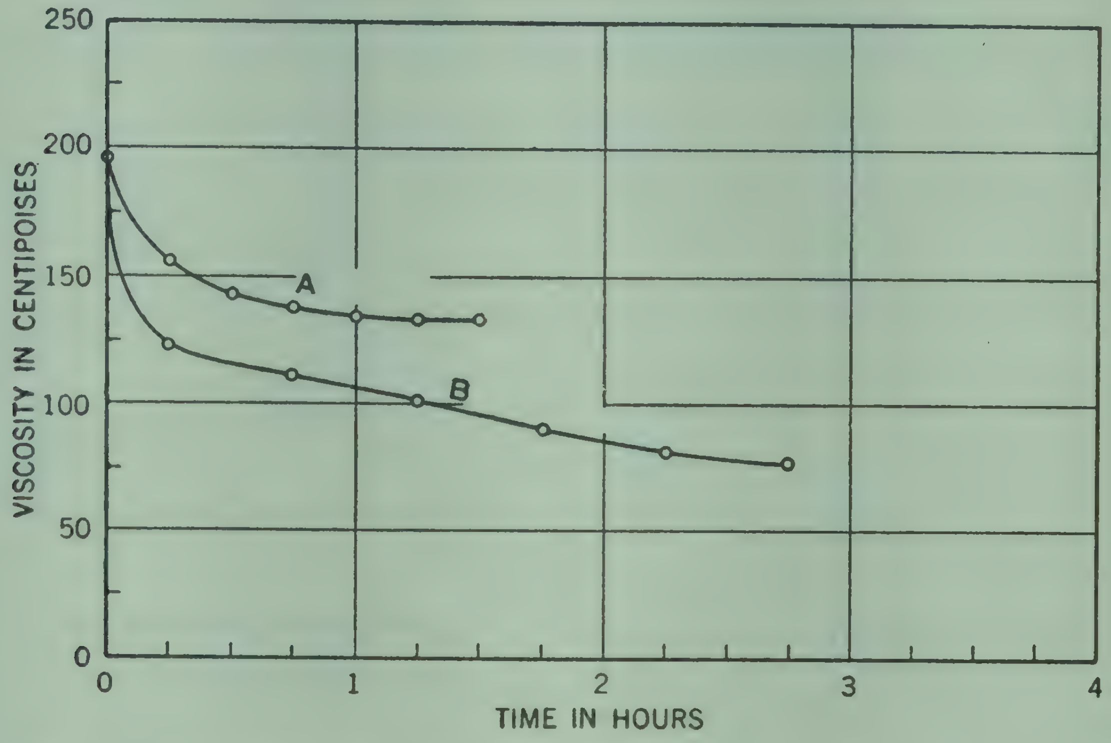

Fig. 2. Viscosities of sulfite pulps treated with chlorine and with hypochlorite. The bleachability of the pulp was 5.3%; the chlorine used was 3.45% in each case. A, chlorination; B, hypochlorite bleaching.

The curves in Figure 2 illustrate the advantage, as far as viscosity retention is concerned, of chlorination over hypochlorite oxidation as the first operation in the bleaching process. The illustration involves two samples of the same pulp, one treated with elemental chlorine in an amount equal to 65% of the test bleachability, and the other with hypochlorite. It should be noted that in the case of chlorination (curve A), the viscosity of the chlorinated pulp has become nearly constant at the end of 1 hr., whereas the viscosity of the hypochlorite-treated pulp (curve B) is not only lower at the end of 1 hr. but is decreasing rapidly.

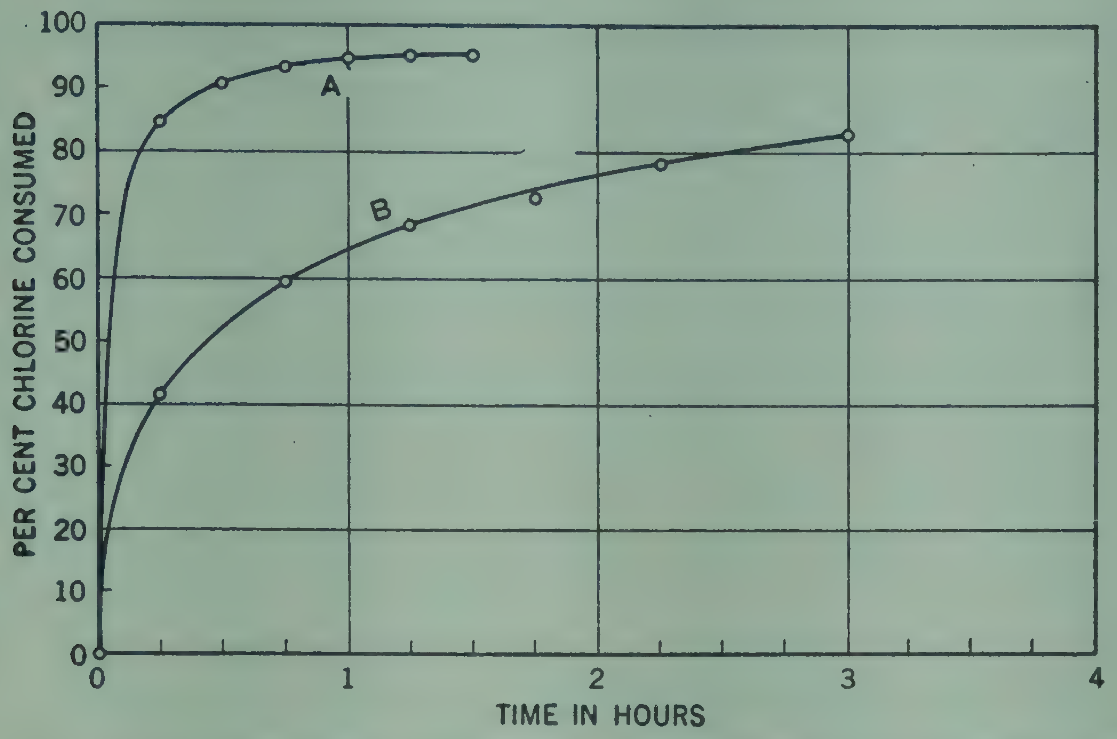

Fig. 3. Comparison of action of chlorine and hypochlorite on sulfite pulp. The points on these two curves were determined on pulp samples taken at the same points indicated on the curves in Figure 2. A, chlorination; B, hypochlorite bleaching.

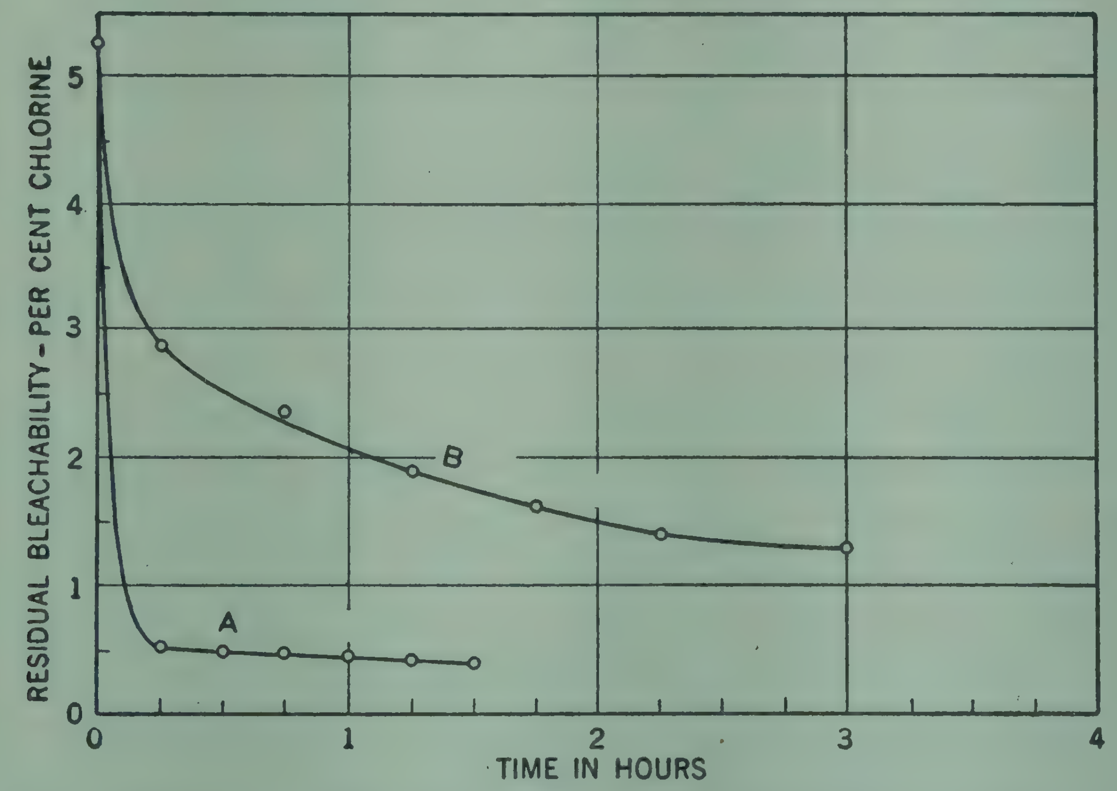

Fig. 4. Residual bleachability of sulfite pulp. The points on these two curves were determined on pulp samples taken at the same points indicated on the curves in Figure 2. A, chlorination; B, hypochlorite bleaching.

The curves in Figures 3 and 4 demonstrate other technical and economic advantages achieved by proper chlorination in the first bleaching stage.

Curve A in Figure 3 indicates that at the end of 1 hr. approximately 95% of the chlorine added has been consumed. If hypochlorite is used instead of chlorine, only about 65% is consumed at the end of 1 hr. (curve B). In Figure 4, curve A (chlorination) denotes a residual bleachability of approximately 0.5% chlorine after 1 hr., whereas curve B (hypochlorite treatment) shows a residual bleachability of 2.0% at the end of this time.

The chief reason why the chlorination of sulfite pulp brings about such a great reduction in bleachability is that the chlorinated lignin residue in sulfite pulp is soluble in the acid solution resulting from chlorination. Thus, these readily oxidized materials are mostly removed and do not consume large quantities of reagent in the hypochlorite bleaching stage. With sulfate and soda pulps these considerations do not apply. The lignin residue of these chlorinated pulps is almost entirely insoluble in the acid solution and must be removed by alkaline extraction. If a sulfate pulp having a test bleachability of 6.0% chlorine is chlorinated with 3.9% chlorine (65% of the test bleachability), the chlorinated pulp after washing will still have a residual bleachability of nearly 3.0% chlorine.

Sulfate pulps made from coniferous woods are generally chlorinated to about 65% of the test bleachability. Exceptions are made in the case of some sulfate pulps prepared from hardwoods where it has been found that chlorination cannot be carried beyond approximately 40% of the test bleachability without severe degradation. In Figure 1 it has been shown that oxidation under acid conditions begins to dominate after about 40% of the chlorine, based on the test bleachability, has been consumed. It appears that the thin-walled vessels prevailing in certain hardwoods are more easily degraded by oxidation in acid solution than are fibers from coniferous woods.

Dodson[13] obtained a patent in 1949 which is said to minimize greatly the drop in viscosity which occurs when pulps are chlorinated under acid conditions. According to this patent, the addition of small amounts of amines, substituted amines, and salts of the amines, as well as chloramines, suppresses the drop in the viscosity of pulps undergoing chlorination. An examination of curve A in Figure 2 shows that sulfite pulp undergoing chlorination suffered a viscosity drop of about 25% in the course of 1 hr. According to the Dodson patent much of this viscosity drop will be prevented by the addition of amines or amine derivatives amounting to from 0.03 to 6.0% of the chlorine used.

Although chlorination is considered a definite part of the bleaching treat-

[13] A. M. Dodson (to Hercules Powder Co.), U. S. Patent 2,478,379 (Aug. 9, 1949); *Chem. Abstracts*, **43**, 9447 (1949).

ment, it should be understood that under normal conditions chlorination is in no sense a bleaching process but rather an extension of the pulping process, the object of which is to render the lignin remaining in the fiber soluble either in acid or alkaline solutions.

2. Alkaline Extraction

In the discussion of the chlorination of sulfite pulp, it was stated that most of the chlorinated sulfite lignin was readily soluble in the acid chlorinating solution. However, the lignin and coloring matter in the medullary ray fiber is not soluble and, though it represents only a small portion (5 to 10%) of the total fiber, it has been found that a mild alkaline extraction following chlorination will remove at least a portion of this material. By washing the alkaline-extracted pulp prior to final hypochlorite bleaching, improved brightness may be realized. The alkaline extraction of sulfite pulps intended for paper manufacture is carried out at either high or low consistency,[14] at prevailing temperatures, and under very mild alkaline conditions. Usually 10 to 15 lb. of caustic per ton of pulp is used for this purpose. For the manufacture of sulfite pulps for cellulose derivatives, more drastic caustic extraction is employed as will be discussed later (see Section D-3 of this Chapter VII).

Since the chlorinated lignin residues in sulfate and soda pulps are not soluble in the acid chlorinating solution, it is necessary to remove as much of this material as possible by alkaline extraction to avoid high concentrations of oxidants in the final bleaching. Cold alkaline extraction is of little value for the maximum removal of the chlorinated lignins of sulfate and soda pulps. The general practice is to extract the chlorinated pulp at a temperature of 65° to 70°C. and at a consistency of 10 to 15% for a period of about an hour. The amount of caustic soda is usually 20 to 40 lb. per ton of pulp. Hot alkaline extraction will, after washing, reduce the bleachability of the extracted pulp enough to permit hypochlorite bleaching in one or two stages without excessive degradation.

3. Hypochlorite Bleaching

The chlorination of sulfite pulp and the chlorination plus alkaline extraction of sulfate and soda pulps result in the removal of most of the noncellulosic incrustants which tend to protect the cellulose against oxidative degradation. However, chlorinated pulp is still colored and must be submitted to some type of oxidation to destroy the color adsorbed on the fiber. For the purpose of destroying this color, many oxidizing agents have been tried, but those which have been adopted commercially are limited by their specific action and their price. The cheapest of all oxidizing agents are the hypochlorites in the form of sodium or calcium hypochlorite, and these are the most widely used in the bleaching of pulp. For special qualities in the finished product, the oxidizing agents sodium peroxide, hydrogen peroxide, sodium chlorite, and chlorine dioxide have been used in increasing amounts in recent years. These special bleaching agents will be considered after the use of the hypochlorites is discussed.

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[14] The consistency of a pulp is defined as the percentage of pulp solids in a measured volume of suspension.

The role of different oxidizing agents in the degradation of cellulose has been covered in Section C of Chapter III. There it is shown that the degradation encountered in hypochlorite bleaching is largely influenced by the pH and temperature of the treatment. The action of hypochlorite at pH 7 brings about a sharp reduction in viscosity and a corresponding increase in the copper number. The reagent becomes less degradative with increasing pH. Under any conditions, hypochlorite bleaching causes some carbonyl and carboxyl group formation in the cellulose molecule. The end products in exhaustive hypochlorite bleaching are carbon dioxide and low molecular weight organic acids.[15] It is evident from the foregoing that careful control of bleaching variables is necessary for the production of bleached pulps of maximum physical and chemical quality.

The final bleaching of sulfite pulp is usually done in one hypochlorite stage, especially if the chlorinated pulp has been given a mild, cold alkaline extraction after chlorination. The consistency is usually held at 14 to 16% and the temperature at 30° to 35°C. If no alkali is present, the pH will droy rapidly to a point where the cellulose will suffer marked degradation (see Section B-1 of this Chapter VII). To avoid degradation it is customary to add enough caustic soda at the start of the bleaching to keep the pH not less than 8.0 during the entire bleaching cycle. An excess of alkali over that necessary to neutralize the acids formed will act to slow down the bleaching action. To avoid this, various buffering agents such as magnesium oxide or alkaline phosphates have been suggested but caustic soda is most generally employed. A slight excess of hypochlorite over that necessary to complete the bleaching is always used because complete exhaustion of the bleach will cause color reversion.

In the case of sulfate and soda pulps, chlorination fails to reduce the bleachability as much as is the case with sulfite pulp. Furthermore, even after hot alkaline extraction, the bleachability is still considerably higher than that for chlorinated sulfite pulp. It is also true that pulps produced by alkaline cooking processes are more easily degraded by oxidizing agents especially if the concentration of the oxidizing agent is high. To avoid high concentration of oxidant, it is customary to divide the bleaching of sulfate and soda pulps into two or more stages with washing between stages. Some mills subject the pulp to a mild alkaline extraction between stages. The temperature, pH, consistency, and excess bleach at the end of the process are the same as in the bleaching of sulfite pulps. It has also been found that treatment of the pulp after the final bleaching stage with a solution of sulfur dioxide or other acid to a pH of 5 to 6 will increase brightness and prevent later color reversion. Furthermore, the acidification of the bleached pulp with sulfur dioxide reduces ferric iron to the ferrous state and lowers the ash content of the pulp.

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[15] H. Rashback and F. H. Yorston, *Quart. Rev.*, Forest Products Laboratory of Canada, No. 7, 12 (July–Sept., 1931).

Although chlorination, hot caustic extraction, and final hypochlorite bleaching yield pulps of satisfactory brightness from most wood species, there are pulps made from some wood species (specifically Douglas fir) which are very difficult to bleach to satisfactory brightness because of the dark color of the pulp after caustic extraction. A modification of the normal process has been found to give very satisfactory results.

The pulp is first chlorinated in the normal manner. Following this it is washed and neutralized at low consistency to give a pH slightly over 7, and then is washed and thickened to a consistency of 10 to 12%. A calculated amount of hypochlorite, equivalent to approximately 80% of the test bleachability of the chlorinated and neutralized pulp, is added together with enough caustic to keep the pH above 8 during the bleaching cycle which, at a temperature of 30°C., is from 1 to 1.5 hrs. The partially bleached pulp is then washed and extracted with 1.5 to 2.0% caustic, based on the pulp, at 65° to 70°C. after which it is washed and given a final bleach in one or two stages. The partial hypochlorite bleach after chlorination gives a pulp, after caustic extraction, of a light buff color instead of a dark brown color, and the final bleaching may be much less drastic.

A similar modification is proposed by Rue and Sconce.[16] According to their method, an excess of chlorine is added to the unbleached pulp and allowed to react for only a short time (5 to 10 min.) after which lime slurry is added to neutralize the hydrochloric acid formed and to convert the excess chlorine to hypochlorite. The hypochlorite is allowed to exhaust in a retention tower or tank, then the pulp is washed, extracted hot with caustic, and bleached. This process is in use in some mills and is said to give satisfactory results. It should be noted, however, that the hydrochloric acid formed during the chlorination must be neutralized with lime whereas, if the correct amount of chlorine is used for chlorination and the pulp is washed in the acid condition, no alkali is consumed for neutralization. Furthermore, lime salts of chlorinated lignin are much less soluble than sodium salts and are more difficult to bleach.

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[16] J. D. Rue and J. S. Sconce, *Tech. Assoc. Papers*, 16, 503 (1933).

4. Chlorine Dioxide and Sodium Chlorite

During the past ten years, chlorine dioxide and sodium chlorite have come into extensive use especially in the final bleaching of alkaline-cooked pulps.[17] Sodium chlorite and chlorine dioxide have lower oxidation potentials than hypochlorous acid, and can act as efficient oxidizing agents for the destruction of color while having a minimum degrading action on cellulose when used under proper conditions of pH and temperature.[18] Figure 5 shows the oxidation potentials of sodium hypochlorite, chlorine dioxide,

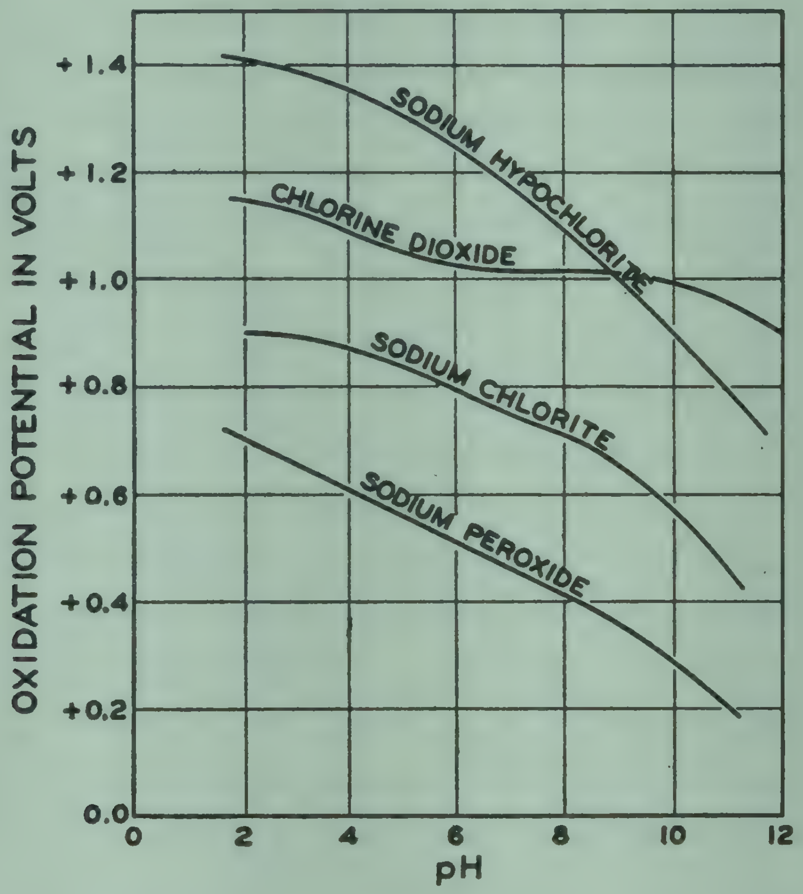

Fig. 5. Oxidation potentials of different oxidizing agents used in pulp bleaching as a function of pH.[19] Courtesy of Solvay Process Division.

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[17] G. Jayme and S. Mo, *Papier-Fabr.*, **39**, No. 33, 193 (Aug. 16, 1941).

[18] O. Samuelson and C. Ramsel, *Svensk Papperstidn.*, **53**, 155 (1950).

sodium chlorite, and sodium peroxide.[19] It should be noted that in the case of chlorite, at no ordinary pH level does the oxidation potential (i.e., oxidative driving force) exceed that of a mild (pH 10) hypochlorite bleach. The use of chlorite under mild acidic conditions permits a selective attack on readily oxidized colored noncellulosic contaminants without damage to the cellulose structure itself. Chlorine dioxide is somewhat less selective but, as the potential curves show, it is considerably safer than hypochlorite in the acid range.

Sodium chlorite was first produced commercially in this country by passing chlorine dioxide into a caustic soda solution in the presence of a suitable reducing agent.[20] The product was sold originally under the name "Textone" and was recommended for the bleaching of cotton textiles to high brightness values. Later the name was changed to "C2" and the product was recommended for the final bleaching of pulps which were difficult to bleach to high brightness without the severe degradation resulting when hypochlorite was used.[21]

Sodium chlorite is a yellowish, readily soluble salt which may be stored and shipped without danger[22] provided it is kept out of contact with organic material. When acidified, sodium chlorite yields chlorous acid and chlorine dioxide which are the active bleaching agents. If only small quantities of chlorine dioxide are needed, sodium chlorite offers a convenient means of storage although it is more expensive than chlorine dioxide generated as it is used.

The most rapid development of processes for the generation of chlorine dioxide on a commercial scale occurred in Sweden.[23] Sodium chlorate in acid solution is reduced by diluted sulfur dioxide gas, and the chlorine dioxide gas is absorbed in water. The chlorine dioxide solution must be used promptly to avoid loss of oxidizing power by decomposition. Chlorine dioxide obtained by this process contains some chlorine, the ratio of chlorine to chlorine dioxide being about 1 to 20. A recent synthesis involves reduction of an acid solution of sodium chlorate with methanol vapor. This process is said to yield chlorine dioxide free of chlorine.

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[19] *The Oxidation Potentials of Common Bleaching Agents*, Research Report 1949, Alkali Section, Solvay Process Division, Allied Chemical & Dye Corp., Syracuse, N. Y., 1949.

[20] G. P. Vincent, *Chem. Inds.*, **47**, No. 3, 280 (Sept., 1940); G. P. Vincent (to Mathieson Alkali Works), U. S. Patents 2,092,944–5 (Sept. 14, 1937); *Chem. Abstracts*, **31**, 8134 (1937).

[21] G. P. Vincent, *Mfrs.' Record*, **109**, No. 12, 34 (1940).

[22] M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, *Ind. Eng. Chem.*, **32**, 899 (1940); J. F. White, M. C. Taylor, and G. P. Vincent, *Ind. Eng. Chem.*, **34**, 782 (1942)

[23] G. Holst, *Svensk Papperstidn.*, **50**, 472 (1947).

Chlorine dioxide bleaching is carried out at relatively high consistency and at temperatures of 50° to 60°C. in closed bleachers to prevent loss of reagent during the bleaching cycle. Then the bleached pulp is treated with sulfur dioxide, which destroys excess chlorine dioxide, and is then washed.

Since the chlorine equivalent of chlorine dioxide costs approximately four times that of elemental chlorine, the use of chlorine dioxide is largely limited to final bleaching only where its unique properties make it of special value in producing high brightness with minimum cellulose degradation.

5. Peroxide Bleaching

Peroxidic materials (hydrogen and sodium peroxides) are of obvious interest as oxidative bleaching agents. However, because of poor availability and lack of suitable techniques, peroxides have not until recently been employed in the chemical purification of wood cellulose. The reagents are now used very successfully in the bleaching of groundwood and semichemical pulps.[24] The low oxidation potential for peroxide (see Fig. 5) denotes a high degree of selectivity. It has actually been established that under ordinary bleaching conditions, very little degradation of cellulose occurs.[25] At the same time, the peroxide potential is sufficiently high to destroy readily oxidized, colored lignin residues. Thus, although the relative cost of these reagents is high, this is offset by the fact that they permit a high degree of whitening of crude wood cellulose furnishes without serious yield loss.

In actual practice certain precautions must be taken to prevent rapid peroxide decomposition. In the presence of large amounts of iron and copper, such as may enter through service water, peroxide decomposition far exceeds the rate at which the furnish may be oxidized. Normally, sodium silicate and magnesium sulfate are added to inhibit this catalyzed decomposition.[26] The additives incidentally have a desirable buffering action.

Although the chief use of peroxidic bleaching is in the instances referred to above, it is known that the technique can be applied as a finishing treatment for previously chlorinated and hypochlorite-bleached chemical pulps. Thus, peroxides are to some extent interchangeable with chlorites and chlorine dioxide.

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[24] J. P. Casey, *Pulp and Paper*, Vol. I, Interscience, New York-London, 1952, pp. 296–302.

[25] H. Staudinger and J. Jurisch, *Papier-Fabr.*, **35**, Tech. Tl., 459 (1937).

[26] J. S. Reichert, D. J. Campbell, and R. T. Mills, *Paper Trade J.*, **118**, 45 (Apr. 13, 1944).

6. The Washing Operation

One of the most important operations in the bleaching process is washing after the different chemical treatments. Soluble residues from any of the operations, if left in the pulp, will interfere with the steps which follow, causing increased consumption of chemicals. Pulp is now washed almost universally on continuous vacuum filters by a combination of dilution washing and displacement washing. Pulp from any of the bleaching steps must be diluted to a consistency of 1 to 1.5% before entering the filter. Modern vacuum filters are capable of discharging a pulp cake having a consistency of 10 to 20%, depending on whether or not press rolls are used. Thus, when a pulp slurry of 1% consistency, having the soluble solids evenly distributed in the aqueous phase, is thickened to a consistency of 10% in passage over a vacuum filter, nearly 90% of the soluble material will pass out with the filtrate. Showers are provided to complete the removal of the soluble solids by displacement washing. The wood cellulose fiber possesses a complex physical structure which shows strong tendencies to adsorb or to hold impurities tenaciously in the minute fiber canals; consequently the washing of pulp is not as simple as the theory of washing would make it appear. Each step in multistage bleaching requires large volumes of water for washing, so countercurrent techniques are employed as far as is practical. The most highly contaminated filtrates, such as those from chlorination and caustic extraction, are sent to the sewer. Fresh water is used for showers on the filters handling bleached pulp, and the effluent from these filters is used for dilution on the next filters in line. By utilizing countercurrent washing, it is possible to accomplish efficient purification in multistage bleach plants with the use of 30,000 to 40,000 gal. of water per ton of pulp bleached. Water for use in the bleach plant must be very low in color, of high clarity, and as free as possible from metal ions, especially iron, copper, and manganese, which, if present, will act as catalysts to degrade the cellulose in the bleaching steps.

C. EQUIPMENT FOR COMMERCIAL CHLORINATION, BLEACHING, AND ALKALINE EXTRACTION

Equipment designed for the chlorination of pulp must be strictly acid resistant since the pH of the pulp slurry, shortly after chlorination is started, drops rapidly to a value between 1 and 2. For alkaline extraction, vessels of plain steel or tile-lined concrete are quite satisfactory. Equipment for hypochlorite bleaching is usually constructed of tile-lined concrete or steel and need not be highly resistant to acid because the bleaching action is normally carried out at a pH greater than 7.

1. Chlorination Equipment

Chlorination at the customary 3 to 4% consistency level may be performed in batch or continuous chlorinators. As pointed out previously, the action of chlorine on either sulfite or sulfate pulp is rapid, and no attempt is made to control temperature. As temperature is increased, the reaction rate increases, but it is necessary only to provide equipment sufficiently large to accomplish the exhaustion of the chlorine in a reasonable time at water temperatures attained during the cold season.

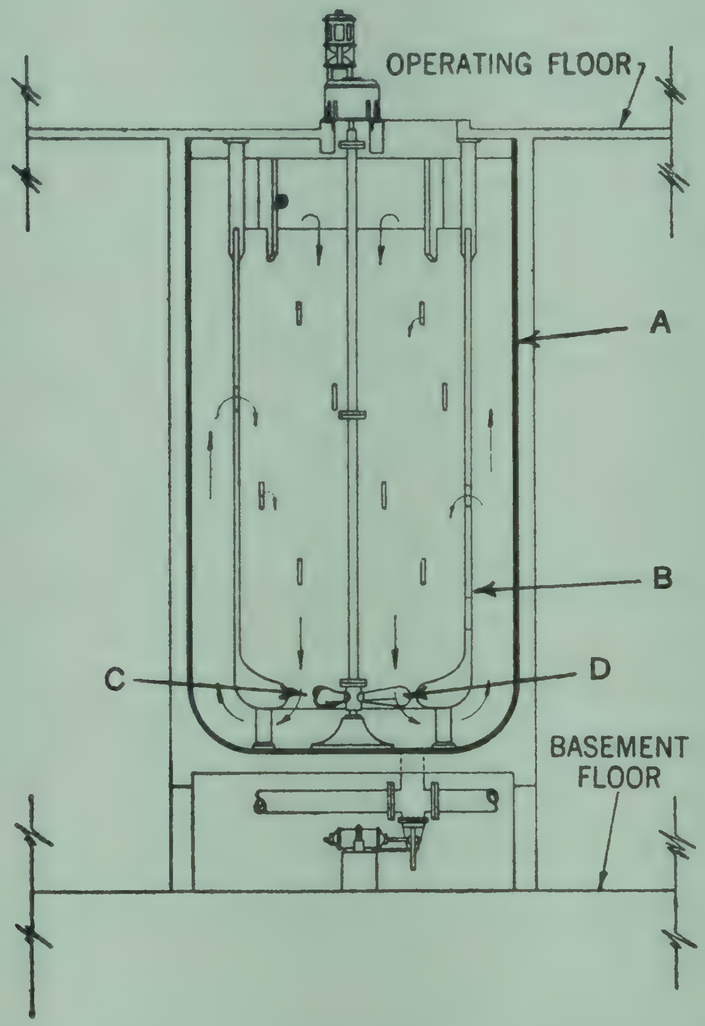

Fig. 6. Type VL batch chlorinator: (A) tank; (B) central draft tube; (C) constricted throat of draft tube; (D) propellor. This chlorinator has been widely adopted in this country for the chlorination of both sulfite and sulfate pulps. Courtesy of Pulp Bleaching Co., Seattle, Wash.

In simple batch chlorination, a known weight of pulp is introduced into a suitable vessel, and a weighed or metered amount of chlorine is bubbled into the slurry over a relatively short period of time. Following this, the chlorine is allowed to react until it is exhausted, and the chlorinator contents are then pumped over an acidproof washer. Figure 6 is an elevation of a commonly used batch chlorinator. This chlorinator consists of a tile-lined concrete or rubber-covered steel tank A and a central draft tube B with a constricted throat C. A propeller D is located in the throat of the draft tube and is designed to circulate the pulp slurry downward through the draft tube and upward around the outside. Chlorine gas from a suitable liquid chlorine evaporator is piped to a point directly above the intake of the impeller or a solution of chlorine in water may be piped to the same point. Chlorine gas may be measured with a flowmeter or it may be delivered from a weighing tank. The chlorinator is filled with the unbleached pulp slurry of known consistency and bleachability. The amount of chlo-

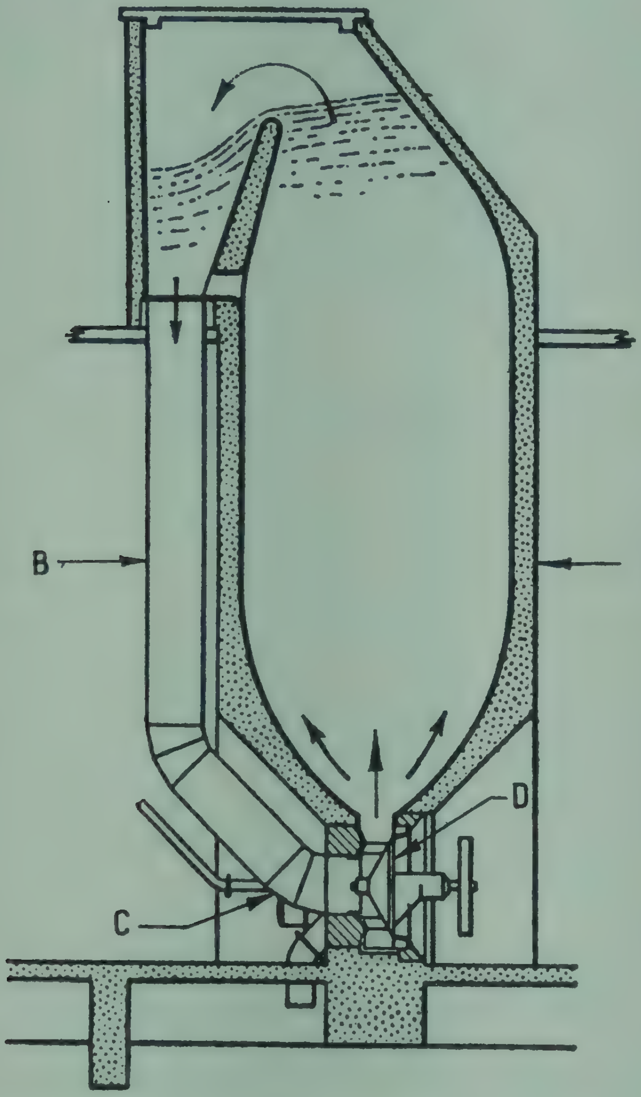

Fig. 7. Kamyr batch chlorinator: (A) tank; (B) external pipe for return of pulp; (C) inlet for chlorine gas or chlorine water; (D) impeller. Courtesy of Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.

rine calculated from the test bleachability is then run in as rapidly as it will be absorbed. At the end of about 1 hr. the chlorinated pulp is pumped to an acidproof vacuum washer and washed free of acid.

The Kamyr batch chlorinator is shown in Figure 7. This chlorinator depends upon a pump instead of an impeller for circulation. The pump circulates the pulp upward through the tank A and the return is through an external pipe B. Chlorine gas or chlorine water is injected at C.

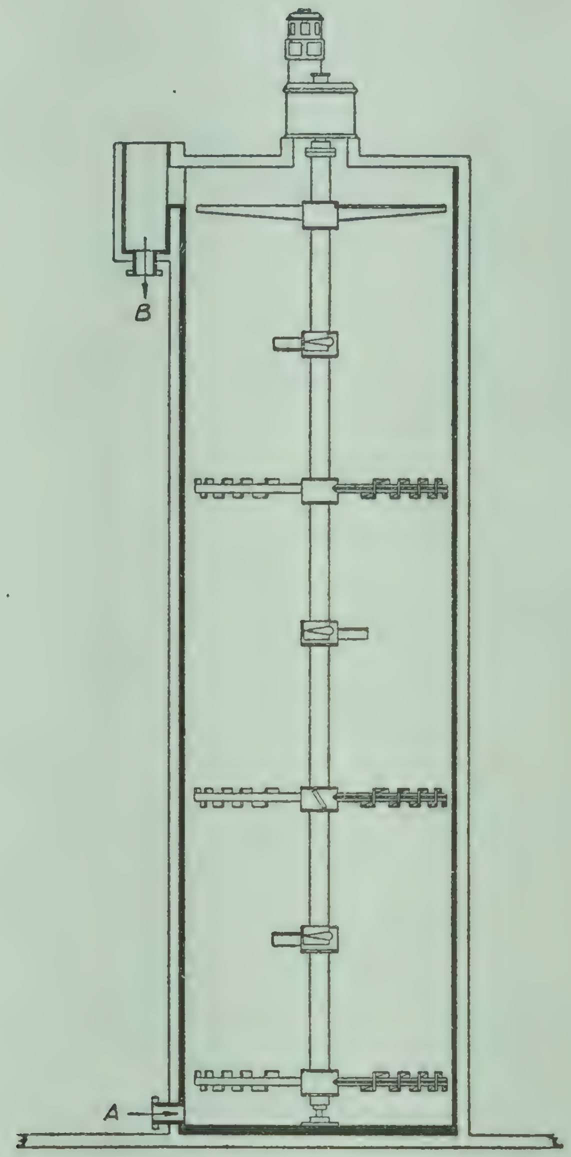

Fig. 8. Continuous chlorinator: (A) point at which pulp suspension mixed with chlorine is introduced; (B) point at which the chlorinated pulp suspension is discharged. Courtesy of Pulp Bleaching Co., Seattle, Wash.

The present trend in chlorination of both sulfite and sulfate pulp is toward continuous methods. Continuous chlorinators are usually vertical towers of sufficient capacity to allow the proper retention time for the completion of chlorination at system rate of flow. They may be constructed of tile-lined concrete or rubber-covered steel. If good mixing of chlorine and pulp is assured, the continuous process is quite satisfactory, and considerable building space as well as power input may be saved. One form of continuous chlorinator is shown in Figure 8. Good mixing of the chlorine with the pulp is secured by injecting the chlorine into the suction of the pump A which delivers the pulp to the bottom of the tower. Intermittent agitation may be supplied by agitating arms located at different levels in the tower. The chlorinated pulp is discharged at the top of the tower through B to a suitable acidproof washer.

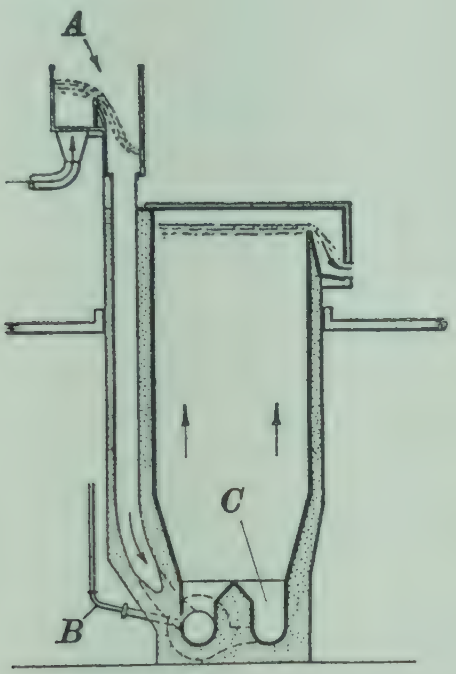

Fig. 9. Kamyr continuous chlorinator: (A) flow box for introduction of pulp; (B) inlet for chlorine; (C) channel for mixing. Courtesy of Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.

The Kamyr continuous chlorinator is shown in Figure 9. This chlorinator has a special agitating zone located in the base of the tower to secure good mixing of chlorine and pulp. Chlorine is injected into the discharge of the pump which feeds the tower, and the mixture of pulp and chlorine is thoroughly agitated in the channel C before rising through the tower and discharging to an acidproof washer.

2. Bleaching Equipment

After either acid- or alkaline-cooked pulps have been chlorinated, they are washed on acidproof vacuum washers. These washers consist of a cylinder, usually of rubber-covered cast iron, and a stainless steel wire covering. The cylinder, with its wire covering, operates either in a rubber-covered steel vat or an acidproof tile-lined vat. After the pulps have been washed, they are caustic-extracted in the case of alkaline-cooked pulps (see topic 3 below) or, in the case of acid-cooked pulps, they may be bleached immediately or given a very mild cold alkaline treatment. In either case, pulps are usually washed again after alkaline treatment. The washing after alkaline treatment is done on vacuum washers which need not be acidproof.

The hypochlorite bleaching stage (or stages) is carried out at a relatively high consistency (usually 16–18%) and as before by a batch or continuous process. One of the widely used batch bleachers is the so-called Type VW, as illustrated in Figure 10. This bleacher was originally developed and patended by Fletcher.[27] The bleacher consists of a cylindrical tank with a hemispherical bottom constructed of concrete or steel and tile lined. A central shaft, on which is mounted a heavy screw conveyor B and a plow A designed to sweep close to the bottom of the tank, is the means of circulation. Openings are provided for charging the bleacher with pulp and chemicals and discharging the bleached pulp into a dilution chest. This

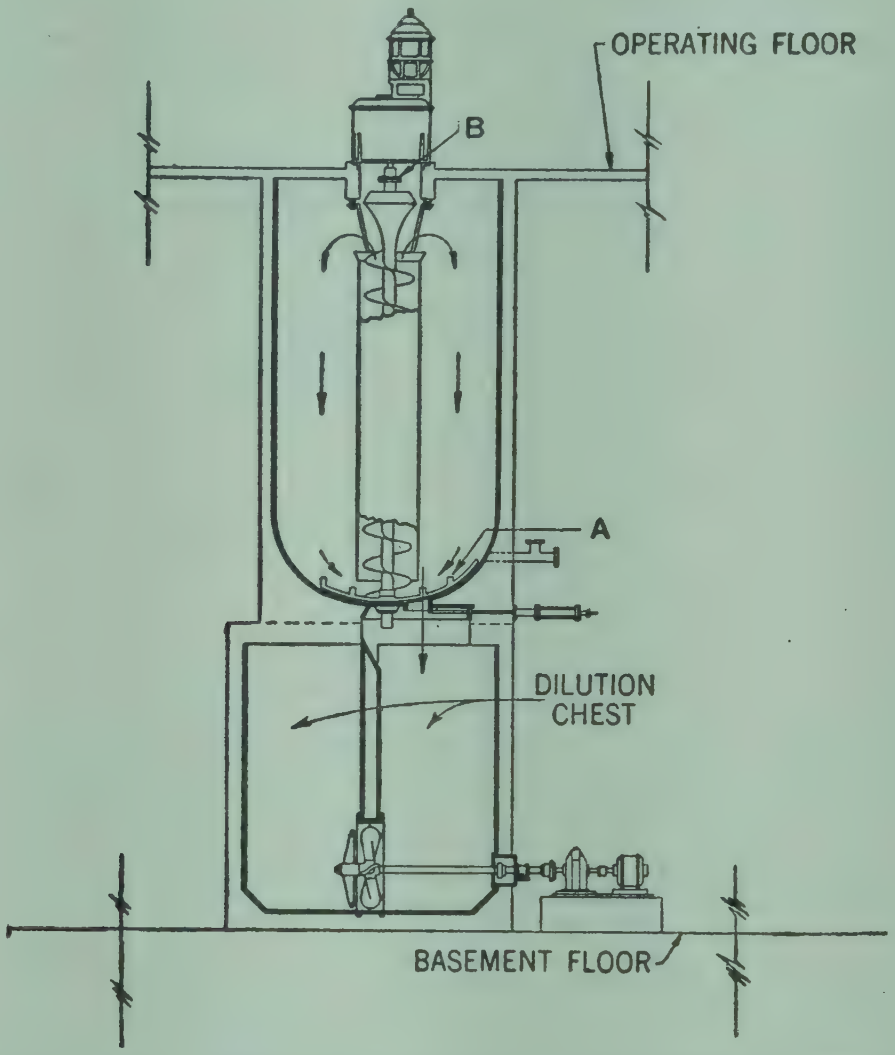

Fig. 10. Type VW batch bleacher with dilution chest: (A) plow designed to sweep close to bottom of tank; (B) screw conveyor. Courtesy of Pulp Bleaching Co., Seattle, Wash.

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[27] P. K. Fletcher, U. S. Patent 1,466,499 (Aug. 28, 1923); *Chem. Abstracts*, **17**, 3790 (1923).

bleacher is capable of circulating 6 to 8 tons of pulp at 16 to 18% consistency in the following manner. The plow A forces the pulp at the bottom of the tank into the screw conveyor which elevates it to the top of the tank where it discharges and returns to the bottom by gravity. Pulp at this consistency loses fluid when mechanical force is applied, thus increasing the solids ratio. Liquid is squeezed out of the pulp as it is gathered by the plow and forced into the screw conveyor. Then, when the pulp is discharged at the top of the conveyor, it absorbs fluid from the surrounding mass and reaches an equilibrium moisture content as it descends again to the plow. Thus, it will be seen that there is a constant turnover of the fluid in contact with the pulp as the circulation proceeds. Moreover, the plow constantly removes a cross section of the pulp as it returns by gravity to the bottom. The net result is an intimate mixing of bleaching fluid with the fiber, with internal friction tending to flex and open up the fiber bundles and expose them to the bleaching action. This method of processing provides a cleaner bleached pulp. The bleachers described operate on a batch cycle of 2 to 4 hrs. and many of them are installed as part of modern multistage bleaching systems.

For batch processing, the bleachability of the chlorinated and washed pulp is determined. The bleacher is filled with a definite tonnage, and bleach liquor, slightly in excess of that required as determined by the bleachability, is added together with sufficient caustic and hot water or steam to complete the bleaching action at a pH not less than 8 and at a temperature of 30° to 35°C.

Shortly after the introduction of the batch bleacher just described, Thorne[28] proposed a continuous unit for high-consistency bleaching. Figure 11 is an elevation of a modern Thorne-type bleacher. This bleacher consists of a tower A built of tile-lined concrete or rubber-lined steel. A double-shaft mixer B, in which pulp, bleach solution, and hot water or steam are intimately blended feeds into the top of tower A, and a scraper C feeds the bleached pulp into a twin discharge screw D and a dilution chest E. The tower A is designed to give sufficient retention time for completion of the bleaching reaction at system rate of flow. After the tower is filled from the mixer B, the scraper and twin discharge devices are started and bleaching proceeds continuously. In a continuous bleacher of this type, no provisions are made for intermittent mixing as in the case of the batch units; consequently uniform processing depends on the intimate mixing of pulp and bleaching solution as they enter the tower.

The Kamyr Machine Works of Sweden has designed a continuous, high-consistency bleacher which does away with the dilution chest and also provides a zone where intimate mixing at low consistency is accomplished before the treated pulp is discharged. An elevation of this bleacher is shown in Figure 12. Pulp, steam, and bleaching chemicals pass into the tower A through the double-shaft mixer B at consistencies of 18 to 16%.

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[28] C. B. Thorne, U. S. Patent 1,656,765 (Jan. 17, 1928).

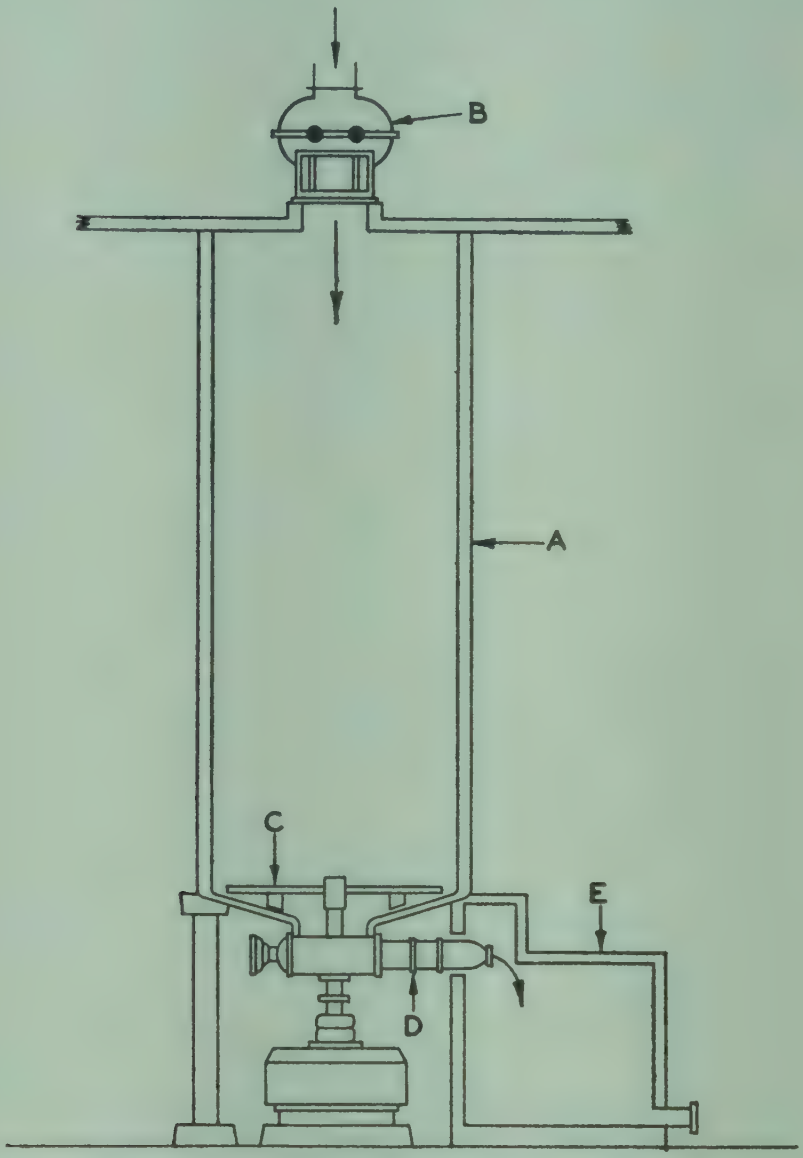

Fig. 11. Thorne-type continuous bleacher: (A) tower; (B) double-shaft mixer; (C) scraper; (D) twin discharge screw; (E) dilution chest. Courtesy of Improved Paper Machinery Corp., Nashua, N. H.

When the tower has been filled, dilution water enters the bottom of the vessel through nozzles C and reduces the consistency to 2 or 3%; a circulating pump D circulates this low-density slurry around the channel E while a discharge pump F withdraws the bleached pulp at system rate of flow. The high-consistency pulp undergoing bleaching floats on the low-consistency bleached pulp in channel E.

The bleachers described in the preceding paragraphs, in one form or another, are used as the hypochlorite stage or stages of modern multistage bleaching systems in which hypochlorite or chlorine dioxide bleaching is preceded by chlorination.

When solutions of chlorine dioxide are used for bleaching, it is necessary that all parts of the bleaching equipment be acidproof because bleaching is carried out at a pH of 4 to 6. Temperatures used in chlorine dioxide bleaching are usually 50° to 60°C. All metal parts of bleachers used for bleaching with chlorine dioxide should be covered with a rubber composition capable of withstanding the operating temperatures. Furthermore, it is desirable to carry out chlorine dioxide bleaching at pressures slightly above atmospheric because of the relatively poor solubility of chlorine dioxide in water.

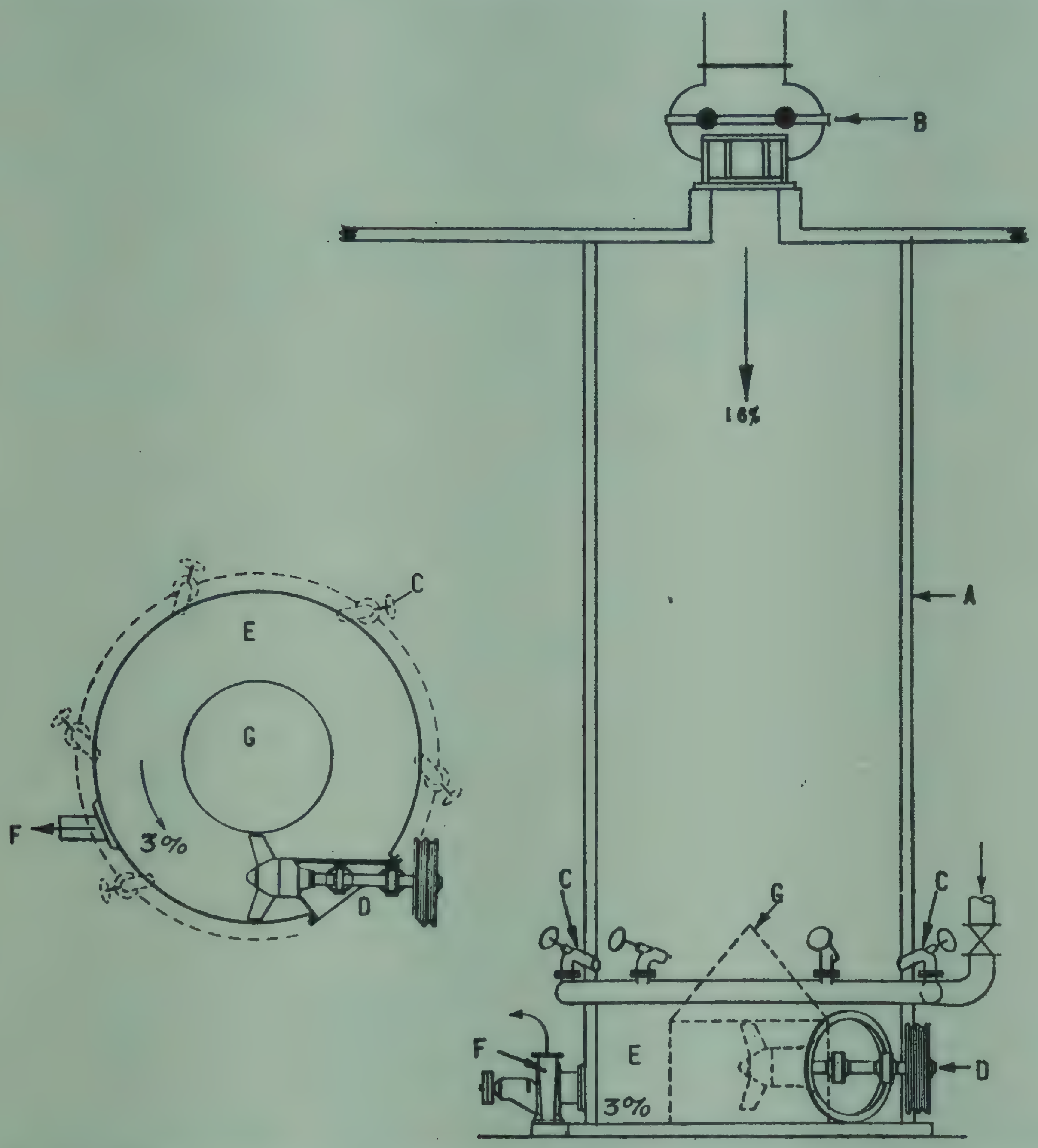

Fig. 12. Kamyr continuous bleacher: (A) tower; (B) double-shaft mixer; (C) nozzles; (D) circulating pump; (E) channel; (F) discharge pump; (G) cylindrical bottom piece with conical top. Percentages represent consistency of the pulp. Detail of bottom is shown at the left. Courtesy of Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.

3. Alkaline Extraction Equipment

The equipment for alkaline extraction is generally of the same type as used for bleaching. For batch extraction, the Type V W bleacher as shown in Figure 10 or one of similar design is used. For continuous extraction, the tower shown in Figure 11 is used to a large extent. The Kamyr Machine Works has developed an ingenious extractor for this purpose as shown in Figure 13.

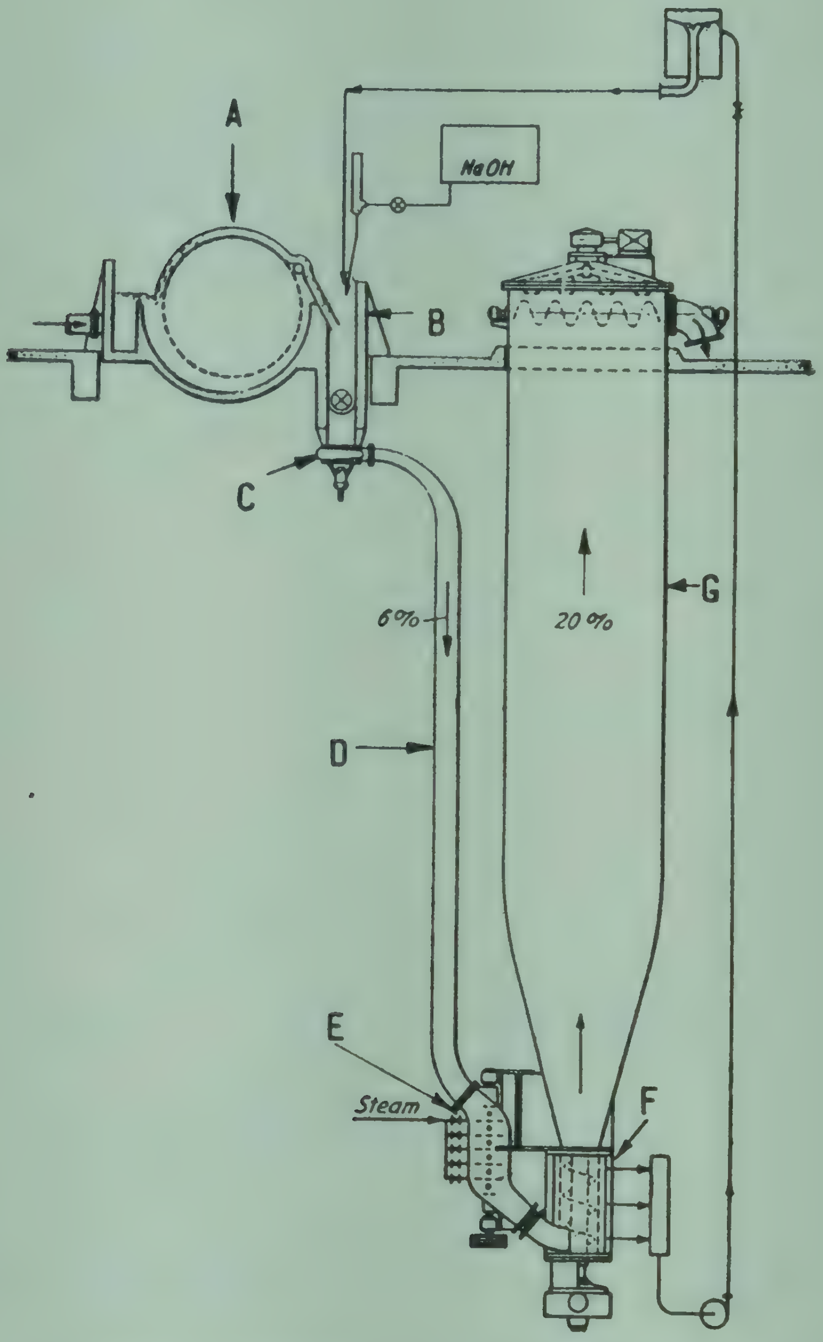

Fig. 13. Kamyr continuous caustic extractor: (A) vacuum washer; (B) mixing trough; (C) pump; (D) pipe; (E) steam mixer; (F) screw press; (G) tower. Courtesy of Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.

The operation of this extractor is as follows: Washed pulp from vacuum washer A is delivered into a mixing trough B, to which both fresh caustic solution and returned caustic are added in predetermined amounts; then the pulp is concentrated to give a consistency of about 6%. The pump C delivers the mixture through pipe D to a steam mixer E and a screw press F at the bottom of tower G. The screw press thickens the hot mixture to approximately 20% consistency. This thickened pulp rises through tower G and is discharged at the top to a washer. The effluent from the screw press is pumped back to trough B for dilution of the pulp from washer A to the desired 6% consistency. Fresh caustic is added here to compensate for the caustic contained in the 20%-consistency pulp rising through tower G. This design of tower is recommended in cases where it is desirable to extract at temperatures above 100°C. This may be done by constructing tower G high enough to give a static head of more than one atmosphere.

D. QUALITY REQUIREMENTS FOR SPECIFIC PRODUCTS

1. Nonpermanent Papers

For most papermaking purposes (i.e., nonpermanent papers), pulps bleached by the methods outlined in the preceding paragraphs are entirely satisfactory as raw material. The chief requirement for such pulps is that they provide papers of adequate physical strength. Minor proportions of retained noncellulosic materials are of no great concern provided that their color contribution has been eliminated by simple and inexpensive bleaching techniques.

2. Permanent Papers

In the so-called permanent papers, the presence of pentosans, hexosans, and short-chain carbohydrate material is undesirable because such contaminants eventually induce discoloration and embrittlement. These papers have been made, in the past, entirely from cotton and linen rags (see Chapter VI-C). The rapid development of synthetic fibers and the increasing use of these fibers in mixture with cotton for a great variety of textiles have greatly restricted the availability of rags as raw material for permanent papers. At the present time there is increased use of bleached cotton linters as well as specially purified wood pulps for this purpose.

The higher degree of sulfite pulp refinement which appears to be necessary in the permanent paper application can be realized by suitable alkaline extraction. In the bleaching of sulfite pulp for most papermaking purposes, the alkaline extraction after chlorination, if used at all, is very mild (e.g., 0.75% alkali based on the pulp at prevailing mill temperature).

For the production of papermaking high-alpha pulp (for permanent papers), the caustic soda concentration is usually 1 or 2% and the extraction temperature is increased to 75–110°C. The conditions of alkaline extraction are ordinarily kept sufficiently mild to avoid excessive yield loss and any adverse effects on beating characteristics. Under certain conditions, however, yield must be sacrificed in the interests of quality.

The equipment used for hot alkaline extraction is the same as that used for normal alkaline extraction. If the extraction is carried out by a batch operation as in a Type V W bleacher, a closed version of this bleacher must be used for operation at temperatures exceeding 100°C. The Kamyr-type caustic extractor previously described (Fig. 13) is capable of operating at temperatures above 100°C. at the bottom of the retention tower because of the static head.

Many attempts have been made to increase the yield of hot-alkaline-extracted sulfite pulp by adding reducing agents such as sodium sulfite or sodium sulfide on the theory that the shrinkage may be due, in part, to the presence of atmospheric oxygen which will attack the resistant cellulose in the presence of alkali at elevated temperature. The alkaline refining of wood pulps has been extensively studied by many investigators. Excellent reviews of this subject have been presented by Jayme[29] and by Rys and Bonish.[30]

3. Purified Pulp for Cellulose Derivatives

Pulp for the manufacture of cellulose derivatives calls for special techniques in the preparation of the unbleached pulp as well as in the bleaching and purification process. One of the most important properties of pulp for cellulose derivatives is reactivity or the ease with which the cellulose undergoes esterification and etherification reactions. Other important considerations involve viscosity, alpha-cellulose content, reducing groups, carboxyl content, and the presence of metal ions. These so-called dissolving pulps are usually cooked to a lower bleachability than is customary for papermaking pulps. The viscosity of the unbleached pulp is also controlled within as narrow limits as practical in the cooking process. In the bleaching process, chlorination follows normal practice. Alkaline extraction is more or less drastic depending on the end use of the pulp. The final viscosity of the bleached pulp depends, first, on the viscosity of the unbleached pulp and, second, on the conditions of the final bleaching. After chlorination, the pulp must have a viscosity appreciably higher than that required in the finished product. The final viscosity is controlled by manipulation of the bleaching variables: temperature, pH, time, and bleach concentration. Acidification of the bleached pulp to a pH of 5 to 6 aids in reducing metal-ion contamination to an acceptable level.

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[29] G. Jayme, *Paper Trade J.*, **106**, 37 (May 26, 1938).

[30] L. Rys and A. Bonish, *Paper Trade J.*, **108**, 31 (May 11, 1939).

Pulps for nitration or for the manufacture of rayon or cellophane are usually given a hot alkaline extraction at temperatures not exceeding 100°C. In actual practice, 3 to 4% caustic based on the pulp will provide in a 100°C. extraction a refined cellulose of the desired alpha-cellulose content (90 to 94%) at over 90% yield.[31] Because of the low caustic proportion and the fact that extensive dilution occurs in washing, caustic recovery is not attempted in an extraction process such as specified above.

Sulfite pulps intended for the manufacture of high-tenacity rayon and for cellulose esters must be purified to an even greater extent. To attain the required high alpha-cellulose content, usually 94.5 to 96.5%, it is necessary to increase the amount of caustic in the extraction process. Caustic proportions of 5 to 12% based on the pulp will provide a wood cellulose of the above purity in a hot extraction (temperature range, 100° to 120°C.).[31,32] However, this caustic concentration at the temperatures specified generally results in a poor yield (70–80% for purification of 86–88% alpha pulp).[31] On the other hand, the alkali proportion is not high enough to necessitate recovery measures.

Practically quantitative yields of refined pulp are obtained by cold extraction with higher caustic concentration. Solutions of mercerizing strength, approximately 17.5% NaOH, will raise the alpha-cellulose content of chlorinated sulfite pulps to above 97%,[31] but under these conditions extensive swelling occurs and in subsequent washing and drying, the fibers collapse and become unreactive. It is therefore necessary to select a caustic solution of concentration such that swelling of the fibers will not exceed a certain maximum value, while at the same time the alpha-cellulose content will be raised to the desired percentage. For example, experiments have shown that a chlorinated sulfite pulp, extracted with an 8% caustic solution at 30°C., will not have been swollen enough to render it nonreactive after washing and drying. Because of the sensitivity to oxidation of cellulose in high-strength alkali, the low-temperature caustic extractions are usually performed in the substantial absence of atmospheric oxygen. Closed vessels are used and air is displaced beforehand by steam injection. It is necessary on economic grounds to recover caustic from such treatments, since an 8% concentration for 10% slurry density represents 1440 lb. of ingredient per ton of pulp. The caustic washed from the purified pulp must be evaporated to the proper concentration and reused until the organic solids content becomes too great. At this point, the material is subjected to dialysis or is evaporated and burned to remove organic contamination. Sulfate white liquor used for cooking in the sulfate process may be utilized to raise the alpha-cellulose content of sulfite pulp to the desired level, and the washings may be sent to a sulfate recovery system in those localities where a sulfate mill is adjacent to the sulfite mill.

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[31] G. A. Richter, *Ind. Eng. Chem.*, **33**, 1518 (1941).

[32] N. W. Coster and R. Vincent, *Paper Trade J.*, **119**, 27 (Sept. 21, 1944).

Manufacturers of cellulose derivatives have shown increasing interest in the use of purified pulps manufactured by the kraft process for conversion into cellulose derivatives. Sulfate pulp cooked by the normal kraft process, even when drastically purified, is not suitable for the manufacture of cellulose derivatives because it is not reactive. The sulfate process, as normally operated, may bring about some type of cross-linkage between cellulose and residual carbohydrates.

It was discovered in 1931 that if wood was first subjected to an acid hydrolysis prior to the sulfate cook, the alpha-cellulose content of the resulting pulp was much higher, and the pulp when purified and bleached was sufficiently reactive for the production of cellulose derivatives.[33] Somewhat later, continued research in Germany led to a practical procedure for this operation.[34] During World War II the prehydrolysis process was operated on an extensive scale in Germany with use of dilute sulfuric acid, solutions of sulfur dioxide, or water at elevated temperatures. The solutions of the hydrolyzate separated from the wood were subjected to fermentation for the production of either alcohol or food yeast.

Prehydrolyzed sulfate pulp is purified by the same general processes as are employed in the bleaching of normal sulfate pulp. The pulp is first chlorinated, then washed and extracted with caustic soda at elevated temperatures. When pulps of high purity are required, the strength of the caustic used in hot alkaline extraction may be as high as 10 to 15%, based on the pulp, with temperatures as high as 120°C.

The alkaline-extracted pulp is then bleached in one or more stages either with hypochlorite alone or with hypochlorite as one stage and chlorine dioxide as a final stage. It is then acidified with sulfur dioxide and washed. This bleaching process will result in a bleached pulp having an alpha-cellulose content of over 94% and sufficiently reactive for the production of various cellulose derivatives.

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[33] G. A. Richter (to Brown Co.), U. S. Patents 1,787,953–4 (Jan. 6, 1931); *Chem. Abstracts*, **25**, 816 (1931).

[34] G. Sirakoff, *Holz Roh- u. Werkstoff*, **4**, 205 (1941); through *Chem. Abstracts*, **38**, 2201 (1944).

4. Groundwood and Semichemical Pulps

For years groundwood made from eastern wood species such as spruce and balsam was sufficiently bright when combined with unbleached sulfite to produce a newsprint of satisfactory brightness. As the newsprint industry moved westward and wood species such as western hemlock were used for the production of groundwood, the resulting newsprint was not as bright as that produced from eastern wood species. Manufacturers therefore attempted to raise the brightness of western groundwood first through the use of reducing agents. The first reducing agents tried were bisulfite solutions. These raised the brightness somewhat but the improvement was only temporary and was not entirely satisfactory. The manufacturers then turned to the use of hydrosulfites, chiefly in the form of zinc hydrosulfite, produced by the action of SO_2 on a zinc-dust slurry. This gave a much greater and more permanent increase in brightness. Zinc hydrosulfite is now being used in some of the western newsprint mills. In the meantime, large-scale production of sodium and hydrogen peroxides has resulted in extensive use of these reagents for the bleaching of groundwood. These compounds produce a much higher brightness and one which is more permanent without materially reducing the yield of groundwood on the basis of the original wood.

The considerations in the bleaching of semichemical pulps are similar to those outlined above, in that it is desirable to achieve a whitening action without serious yield loss. Accordingly, peroxides are used widely in purification of semichemical pulps. Some work has been done on the bleaching of such materials with a combination of mild chlorination followed by peroxide bleaching. Under these conditions the yield suffers to some extent but higher brightnesses are obtained.

E. NEW TRENDS

1. Use of New Reagents

It is doubtful if any fundamentally new lower cost methods of producing chemical pulps will be developed for some time. Both the sulfite and alkaline cooking processes have been advanced to the point where maximum recovery of the cooking chemicals may be accomplished. Also these chemicals are low in initial cost. As an additional economy feature, the organic material dissolved from the wood can be utilized as fuel for production of steam and electricity. A similar situation prevails with regard to semichemical pulps since in their preparation the same chemicals are used except in reduced proportions.

The bleaching process has until comparatively recently been confined to the use of hypochlorites, which are still the cheapest oxidizing agents available. During the past decade, the development of successful methods for production of chlorites and chlorine dioxide has led to increasing use of these oxidizing agents because of their unique properties of destroying colored material in highly refined wood cellulose without inflicting severe degradation. Under the most favorable conditions, the cost of these oxidizing agents is much higher than the cost of hypochlorites. Nevertheless chlorites and chlorine dioxide have found, and will continue to find, a place in the industry in instances where exceptional brightness with minimum degradation is the objective. These two reagents are logically applied in finishing techniques for pulps which have already been bleached under mild hypochlorite conditions. It is improbable that these reagents will be applied in the near future to relatively crude wood celluloses because of their high cost. It is known that certain mixtures of chlorite and hypochlorite[35] or mixtures of chlorine and chlorine dioxide[36] can be used under slightly alkaline conditions to provide efficient and relatively nondegradative bleaches. The mechanism of interaction of reagents in the two instances referred to is not completely understood. Insofar as carefully controlled dilution of the more expensive reagents with hypochlorite or chlorine gives about the same effect as use of chlorite or chlorine dioxide alone, there is an important economic advantage to be gained by these techniques. Such processes will certainly be used to an increasing extent in the years to come.

Peroxide bleaching of semichemical or groundwood pulps has been developed extensively in recent years.[24] The peroxides, as reagents new to wood pulp technology, have proved to be excellent bleaching agents in these applications. Peroxide bleaching of these relatively crude forms of wood cellulose will continue to be the subject of active investigation. Also it is likely that peroxides, together with chlorine dioxide and chlorites, will find increasing use as final-stage bleaching agents in multistage purification processes.

[35] G. P. Vincent, L. E. Russell, and V. Woodside, *Paper Trade J.*, **121**, 25 (Nov. 15, 1945).

[36] G. P. Vincent, *Paper Trade J.*, **124**, 53 (June 26, 1947).

2. Continuous versus Batch Processing

The tendency of modern chemical engineering practice is constantly away from batch operation toward continuous operation. This trend is very marked in wood pulp processing. Chlorination is now almost universally carried out as a continuous process. The treatment is always performed at a fluid consistency, and with efficient mixing there is sufficient time for very uniform chlorination of the lignin remaining in chemical pulps. Caustic extraction may also be accomplished by a continuous process, and satisfactory results are obtained by this means. When the bleaching process was confined to the use of hypochlorites alone, intimate mixing of fibers and bleaching agent was essential for a uniform result. The chlorination process has, to a great extent, reduced the differences from fiber to fiber, and continuous bleaching processes are being more universally adopted. If there is sufficient mixing and flexing of the fiber bundles during the bleaching operation, entirely satisfactory results may be obtained at high slurry density in a continuous process, particularly if more than one bleaching stage is employed.

Continuous bleaching systems can be operated with lower power input and require less building space. On the other hand, batch systems have been so designed that the batch bleachers serve as building columns and offer ample room for installation of the necessary facilities for multiple washing. In the final analysis, there is little doubt that continuous bleaching systems will completely supplant batch bleaching.

3. Chemical Control

The chemical control of bleaching systems is relatively simple and rapid, and accurate methods for the determination of bleachability throughout the process are well established. The maintenance of temperature and pH through the use of automatically controlling instruments has greatly simplified bleach plant operation. Rapid methods for the determination of viscosity throughout the bleaching process have been developed and enable the bleach plant operator to control the final viscosity of a given pulp through the use of suitable charts or nomographs.

As a result of all of these modern chemical and engineering tools, the processes involved in the bleaching and purification of wood cellulose have been simplified to the point where product quality is readily controllable.

Chapter VIII

PROPERTIES AND TREATMENT OF PULP FOR PAPER

James d'A. Clark

Almost all cellulose that is produced for the market appears in sheet form from which it is converted mainly to paper or board. Purified pulps and cotton linters intended for chemical purposes are also conveniently handled as sheets. For most chemical purposes, and after conversion into paper and board, the strength and behavior of the sheet both dry and wet are of interest. The marked changes occurring in pulp during "beating" (i. e., the process in which natural cellulose fibers in the presence of water, are pounded, rubbed, or otherwise subjected to mechanical action) and during preparation for sheet formation, are discussed in considerable detail in this chapter. Supplementing this discussion are brief descriptions of the main types of beating machinery and an account of several theories which have been advanced to explain the action of this equipment, which is of great technical importance. One theory—a composite of several theories—will be applied to interpret the effects of beating and allied phenomena on the fibers, pulps, and papers. Brief mention will also be made of the influence of the chemical composition of the pulps on their papermaking performance.

Those who are interested primarily in cellulose reactions should not dismiss lightly this chapter on the qualities of pulps which impart different properties, such as strength, to paper. The forces that hold two fibers together in paper are essentially the same as those that hold the fibrils together in an individual fiber. Conditions of drying and the cohesion of the elements that lead to a strong sheet of paper also make a fiber more difficult to swell and less reactive.

A. PHYSICAL PROPERTIES OF PAPER PULP

Paper is made from a water suspension of less than 0.5% of suitably prepared fibers, by continuously flowing it onto, then draining the water away through, a traveling, endless, fine-meshed screen called the "wire." Usually modifying materials, such as size, papermaker's alum ($Al_2(SO_4)_3$), color, and mineral filler (often china clay) are added to the fiber mixture before dilution. After draining, a matted or felted web of wet fibers remains on the wire from which additional water is removed by suction. The web is then carried by an endless woolen "felt"—actually a woven blanket—through two or three pairs of press rolls to squeeze out as much more water as is possible. The remaining water, now present to the extent of about twice the weight of the fiber, is evaporated as the web is pressed against the successive smooth surfaces of revolving, steam-heated cylinders by an endless, porous "dryer felt." The dried web, usually containing from about 3 to 8% of moisture, passes between calender rolls to smooth it, after which it is wound into rolls (reeled up). One or both sides of the web may be coated either on the paper machine or afterwards, to provide a special surface for printing or other purposes.

The characteristics of the finished paper are influenced by each step in the process, but the main factors are the type of fibers used and especially the manner of preparing them. So far, the evaluation of the quality of pulp by the industry has been largely empirical. Besides estimation of the whiteness (brightness) of the pulp and its cleanliness, the usual method consists of making the pulp into sheets after one or more degrees of beating and subjecting the resulting sheets to physical tests normally applied to paper.[1] Measurements made are basis weight (i. e., weight per unit area, for pulp usually expressed in grams per square meter), resistance to bursting and tearing, and less frequently folding endurance, tensile strength, and permeability to air. An arbitrary measure of the ease of draining water from the prepared pulp suspension is also often made.

As would be expected, desirable qualities of a pulp depend largely on those of the paper into which it is to be transformed. Most paper made is subsequently printed, and when under the pressure of the block in common letterpress printing, it should have a smooth, even, ink-receptive surface. This calls for a sheet having uniform thickness and density, so that when viewed against the light, its appearance should approach that of milky glass and not be "wild" or mottled. Smoothness of surface and ink receptivity are more readily obtained by using pulp having thin fibers; also, the shorter the fibers are, the easier it is to secure a good formation or "look-through." When shorter fibers are used, the strength of the sheet is decreased. However, unlike papers for wrapping purposes, a high

[1] A comprehensive discussion of paper tests may be found in J. P. Casey, *Pulp and Paper Chemistry and Technology*, Vol. II, Interscience, New York-London, 1952.

strength is not essential for printing papers, so that finely ground wood, reworked waste paper, soda pulp from deciduous or hardwood trees like poplar, gum, and birch, and from esparto grass, all of which have an average length in the order of 1 mm., constitute the bulk of the "furnish." Wrappers and other papers that must have a high strength to withstand applied forces are commonly made from coniferous or softwood trees such as spruce, pine, hemlock, and fir, which initially have average fiber lengths in the order of 3.5 mm. Fibers from some of these species, for example, most southern pines, are inclined to be not only longer but also relatively coarser, which makes them less well suited for conversion into fine printings. Cotton, and especially bast fibers such as linen, can be readily beaten so as to split lengthwise into fine and relatively long fibrils and thus may be converted into very fine-textured, strong sheets such as for currency, fine writing, and cigaret papers. As an example of a special requirement, pulp for cigaret papers is usually prepared from flax because of the better smell and taste of its smoke; also, to make the sheet made from the well-fibrillated fibers soft and porous, it is "filled" with about 30% of precipitated chalk.

1. The Strength of Paper

In the pulp and paper industry, "strength" has no definite meaning except the ability of the paper to withstand one or more kinds of applied force. In North America, standard paper tests are carried out with the specimens conditioned in an atmosphere of 50% relative humidity and 73°F.; elsewhere, these tests are run often at the old standard of 65% relative humidity and a slightly lower temperature.

The least complex strength test, the tensile breaking load, is determined by applying a gradually increasing pull to a strip of paper, usually 15 mm. wide and 180 mm. long, at such a rate that a break occurs in about a quarter of a minute. The percentage of elongation of the strip before fracture—that is, its "stretch"—is often measured simultaneously.

When a pull is applied to a strip of paper, the resisting components are the structure itself and the individual fibers. The fibers lie mainly in the plane of the paper and are intertwined, kinked, and twisted. Provided that mutual contact was made while the fibers were wet and was not brought about by calendering after the sheet was dried, the joints extend over an area and cohere to a degree governed by the nature of the fiber, its preparation, and the way in which the paper was made. When a small tensile force is applied to the paper strip, an almost perfectly elastic and recoverable strain will result, corresponding to the unbending or uncurling of the component fibers as happens with a woven fabric. A greater pull will cause more unbending, but soon in one or two places the joints between two fibers, one of which is being particularly stressed by the applied load, will break, thus introducing a small irrecoverable strain in the structure. If the pull is increased to break a number of joints and straighten out more fibers in its direction and then is removed, many of the displaced fibers will require a considerable time to assume their relaxed position. The shrinkage due to this factor constitutes a delayed recoverable, or frictional, elastic strain. Also, as the pull is progressively increased, any fiber that has been straightened out and aligned in the direction of the pull will prevent a further stretching of the structure until it is either pulled loose or broken. The position of such a heavily stressed fiber is analogous to that of a very tough earthworm being tugged from its hole by a robin. If the tugging has proceeded for some time with such meager results that the robin releases the worm, the part of the worm outside of the hole will snap back for a distance corresponding to the elastic strain; the part in the hole and, to a minor extent, the upper part of the worm will contract more slowly for a distance corresponding to the delayed recoverable strain; the distance that the lower end of the worm was elevated by the robin, together with the extent that the worm may have been permanently stretched, constitutes the nonrecoverable strain.

The changes inside the noncrystalline or amorphous regions of a fiber submitted to a pull are probably similar to those in the stressed strip of paper. The molecules and crystallites in these regions correspond to the fibrils and the individual fibers in the paper. One difference is that in a fiber the individual structural elements are almost parallel to each other in each of the various concentric zones. This subject is dealt with more fully in Chapter IV-B.

After the development and use of a new testing instrument of ingenious design, Steenberg[2] and coworkers,[3–5] at the Swedish Forest Products Research Institute, published a comprehensive study of stress–strain–time relationships of paper which has done much to focus attention on the viscoelastic properties of paper. Because of these properties, the strength of paper determined at normal loading speeds should not be relied upon to assess its resistance to sudden shock loads nor to prolonged stress below the breaking load. Rance[6] showed that strips of paper having a tensile strength of 10 kg. under normal testing conditions broke after 14 hrs. under an applied load of 8 kg.; after 20 days under a 6-kg. load; and after 220 days under a 4-kg. load. A summary with some other applications of a study of stress–strain–time relationships has been published.[7]

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[2] B. Steenberg, *Svensk Papperstidn.*, **50**, 127 (1947).

[3] B. Steenberg, *Svensk Papperstidn.*, **50**, 346 (1947).

[4] B. Ivarsson and B. Steenberg, *Svensk Papperstidn.*, **50**, 419 (1947).

[5] B. Ivarsson, *Svensk Papperstidn.*, **51**, 383 (1948).

2. Common Tests for Paper

The outcome of the common physical tests for paper is dependent on the basis weight of the sheet, usually expressed as pounds per 500-sheet ream of a certain size, often 24 by 36 in. The bursting test, the most frequently used test, is made by clamping an area of the sheet, effectively 1.24 inch in diameter, against a rubber diaphragm and applying increasing hydraulic pressure beneath the diaphragm until the paper bursts. The maximum pressure attained is the value reported. The bursting strength more or less parallels the tensile strength in the direction in which the paper has the least stretch, usually the strongest direction of the paper. The ratio of bursting strength to tensile strength increases with the ability of the paper to stretch.

The tearing resistance is found by a pendulum type of instrument which measures the work done to tear several sheets through a fixed distance and is reported in terms of force (in grams) required to tear a single sheet. The measured work also includes bending the specimen and rubbing the torn edges past each other. The result depends mainly on the length of the fibers, on the bulkiness of the sheet and its stretch, and for weak sheets on the degree of fiber cohesion. For a sheet of fibers that do not cohere well, the tear increases as the cohesion between the fibers is increased by any means, until the cohesion becomes sufficient to dissipate the applied tearing force over an appreciable area around the point where the tear is progressing. After this degree of cohesion is reached, a further increase serves to diminish the tearing resistance, usually quite rapidly, because increased cohesion beyond the optimum for tearing resistance has an effect similar to increased sheet density; both serve to concentrate the applied tearing force over a smaller area of the sheet and thus make it more effective.

The folding endurance of a sheet of paper is the number of double folds that a strip 15 mm. wide and under a tension of about 1 kg. will withstand over a line across its width until fracture. The result is dependent on the third or fourth power of the applied tension, so that folding endurance as measured by current methods is unduly sensitive to the normal tensile strength of the strip. True folding endurance is dependent mainly on the length and fineness of the fibers, their elasticity, and on the stretch of the sheet.

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[6] H. F. Rance, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **29**, 449 (1948).

[7] B. Steenberg, *Pulp & Paper Mag. Can.*, **50**, No. 3, 207 (1949).

The air resistance, the inverse of air permeability, is usually measured in terms of the number of seconds for 100 cc. of air, under pressure of about 12 cm. of water, to flow through 1 sq. in. of paper. It depends on the density of the sheet and on the specific surface (i. e., the exposed surface per gram) of its components.

It has long been known that when a sheet of newly formed paper has been dried under tension, as when clamped against a polished plate instead of being allowed to shrink freely while drying, the tensile strength is increased by about 10 to 50%, and the stretch to the breaking point is diminished by nearly 50%. The loss of stretch is mainly due to the removal of the nonrecoverable component. There is also a corresponding drop in bursting strength of 10 to 20%, a decrease in tearing resistance of up to 50%, and usually a severalfold increase in folding endurance. In consequence, paper tests made on pulp test sheets give highly arbitrary values which depend on how the pulp was prepared, how the sheets were formed, and how they were pressed and dried.

Interpretations of such common tests are not only quite complex, but at best merely serve to indicate whether the pulp is more or less suitable for a given paper; they give little information concerning the underlying causes for one pulp to be better or worse than another in any respect. Occasionally, to supplement these physical data, measurement of viscosities and such chemical tests as alpha-, beta-, and gamma-cellulose content, copper number (ability to reduce Fehling solution), and chlorine demand are made. However, as will be briefly discussed later, unless the results are extreme, chemical tests by themselves do not provide a good measure of any papermaking quality of a pulp.

3. Pulp Testing

A more fundamental approach to pulp testing is needed, and one[8] which has shown some promise involves consideration of six pulp qualities rather more basic than those just discussed. However, it should be emphasized that producers and consumers of pulp are mutually restrained from the easy abandonment of orthodox methods, so that up to the present, only meager progress in this direction can be recorded. The following qualities were chosen, not because they necessarily represent the best for the purpose, but because as a group they comprise a fairly complete characterization of the papermaking qualities of pulp which can be deduced from a practical system of currently available measurements. The factors involved are (a) fiber length, (b) dry fiber flexibility, (c) wet fiber flexibility, (d) cohesion, made up of (1) the extent of the area in bonded contact and (2) the intensity of the bonding, (e) intrinsic strength of the fibrous material, and (f) ability of the pulp to respond to the wet mechanical treatment or beating. Of these factors, beating is one of the most important because of its pronounced effects on most of the other factors. For example, an appropriate beating treatment, without the addition of supplementary materials to the pulp furnish, can so modify fiber length, flexibility, and area of cohesion that an average pulp may be made into such extremes as a fairly satisfactory blotting paper or a fairly good transparent greaseproof wrapping paper. The nature and measurement of the first five factors involved in this newer concept of fiber quality will be discussed before beating.

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[8] J. d'A. Clark, *Pulp & Paper Mag. Can.*, **49**, No. 10, 202 (1948).

(*a*) *Fiber Length*

Even today there is no general agreement as to what may be meant by the "length" of fibers in a pulp, mainly because there is a choice of expressing it in a variety of ways, including the numerical average length of the fibers (which is much affected by the lower limit of the length of the particles considered to be "fiber") and the weighted average length by length, by projected area, by volume, and by true weight. Thus the "average" fiber length of untreated black spruce fibers has been reported to vary from 0.74[9] to 3.48[10] mm., usually without definition of the type of average employed. Perhaps because of this uncertainty, as well as the tediousness of making individual fiber measurements, fiber length has been a test somewhat in disrepute. It is clear that just as the molecular length of cellulose affects the strength of the structure it composes, so the length of the fibers affects the strength of paper. Although the number-average length seems to determine the strength of polymers (see Chapter XI), the weighted average length by weight (which will be hereinafter termed "weight-average length") was shown by Clark[11] to be the important one in the case of paper, perhaps because the individual fibers, unlike molecules, vary in thickness and especially because in a test sheet of paper the fibers are isotropic, lying equally in all directions. He found if L was the weight-average length either of the longest fraction of wood pulp fibers separated out, cut, and reclassified, or of rayon fibers cut to various lengths, the tensile strength of test sheets varied as $L^{1/2}$, the burst directly with L, and the tearing resistance as $L^{3/2}$. Some confirmation of these ratios is indicated in a subsequent study[12] by the U. S. Forest Products Laboratory. Fiber length had no measurable effect on the density of the paper nor, contrary to an erroneous common conception which widely persists, on the ease with which water drained from the pulp. Also, if the thickness of all fibers was held constant and if equal weights of uniformly long and short fibers were mixed, the test results on paper made from the mixture corresponded closely with tests on a sheet made from uniform fibers having the same weight-average length as the mixture and did not correspond at all with tests on a sheet made from much shorter uniform fibers having the same number-average length as the mixture.

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[9] J. B. Calkin, *Paper Trade J.*, **91**, 44 (Aug. 28, 1930).

[10] C. D. Mell, quoted by E. Sutermeister, *The Chemistry of Pulp and Papermaking*, 2nd ed., Wiley, New York, 1929, p. 57.

[11] J. d'A. Clark, *Paper Trade J.*, **115**, 36 (Dec. 24, 1942).

These findings are at variance with several previously reported results on the effect of fiber length except one,[13] but in all the other previous findings with that exception, the test specimens were prepared after classifying a whole pulp into portions. There is a significant correlation between the length of a natural fiber in a pulp and its thickness,[14] so it is believed that most of the effects of varying fiber length reported were masked by the important influence of accompanying changes in fiber thickness. The importance of thickness is evident because the flexibility of a rod of circular cross section varies inversely as the fourth power of its diameter, and the number of fibers in a unit area of a sheet of paper of a given basis weight varies as the square of their diameter.

The weight-average fiber length (see TAPPI method T 223 sm-53) is conveniently determined from the fiber distribution with a classifier of the Bauer-McNett type[11] or more rapidly with the Clark Four-Screen Classifier.[15] The specimen fibers, highly diluted in water, are caused to flow through a series of compartments parallel to the faces of screens of decreasing mesh. If the fibers are shorter than twice the screen opening they can turn a somersault on the edge of an opening and pass through. Otherwise they remain in the compartment ahead of the screen. However, fibers longer than twice the size of the openings in the screens may pass through if the fibers are bent or if they are very flexible, so there is always the likelihood of a small error in the determination of length distribution curves and weight-average lengths, unless this effect is measured and allowed for.

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[12] *Sulfite Pulp for Paper*, U. S. Forest Products Laboratory, Mimeographed Report **1596** (1943).

[13] R. B. Brown, *Paper Trade J.*, **95**, 145 (Sept. 29, 1932).

[14] J. H. Graff and R. W. Miller, *Paper Trade J.*, **109**, 31 (Aug. 10, 1939).

[15] A. E. Reed and J. d'A. Clark, *Tappi*, **33**, 294 (1950).

(*b*) *Dry Fiber Flexibility*

Dry fiber flexibility may be defined as the deflection of a dry fibrous element which results from an applied bending moment. It depends markedly on the thinness of the element and its walls, and to a lesser extent on humidity. Fibers are usually tubular, and when the fibers are dried, the sides of most thin-walled fibers collapse to form flat tubes; they therefore bend much more easily, are more flexible, and compact together better than do thick-walled fibers.

In most trees, especially conifers, the summerwood fibers are thick-walled and stiff; the thin-walled springwood fibers, though of equal diameter tangentially and of even greater diameter radially, are more flexible. Paper made from the former is bulky, weak, and brash; paper made from the latter is relatively dense, strong, and pliable. The thin-walled fibers, although individually weaker than the thick-walled fibers, are more numerous in sheets of the same basis weight. Thus they distribute a force applied to the sheet over a greater area and use their strength to greater advantage by virtue of their greater flexibility as well as their greater bonded area.

Since the solid cellulosic material in common papermaking fibers does not vary greatly in its resistance to bending, an approximate measure of dry fiber flexibility is that of the total length of a gram of fiber. This can be ascertained[11] in about half an hour by optical projection; cumulative measurements are made on a fiber suspension of known dilution and volume which has been immobilized by the addition of a gel.[15a] Another approximate measure of dry flexibility is a determination of the average diameter and wall thickness of the fiber from direct measurements of cross sections made on the unpulped fibrous material, for example, wood. These are neither difficult nor tedius to make if a photomicrograph of known enlargement of a representative cross section is available.

Because dry fiber flexibility is closely related to fiber fineness, a measure of either property provides a fair index of the relative surface smoothness and ink receptivity of paper made from the pulp, if an allowance is made for the possible splitting of the fibers by subsequent treatment.

[15a] See TAPPI method T 232 sm-53.

(*c*) *Wet Fiber Flexibility*

Wet fiber flexibility is influenced not only by the factors which govern dry fiber flexibility, but also by the extent to which the fibers were bruised or internally split and fibrillated, or rubbed or externally split, during beating. These factors are not important in dry flexibility because in most cases the split fibrous elements rebond as they dry.

The ease with which fibers are flexed when wet is most conveniently measured by the apparent density (or its reciprocal, the apparent specific volume) of pulp test sheets after these have been wet-pressed and dried without pressure on a polished metal disk in accordance with the standard pulp testing method (TAPPI Standard T 205 m-50). Alternatively, the apparent density may be measured indirectly by the free shrinkage of the pressed moist sheet when dried in the air. As water leaves a freshly deposited moist sheet of paper, adjacent fibrous elements are drawn together by surface tension. Campbell[16] has pointed out that the force involved is independent of fiber thickness and, in consequence, may amount to thousands of pounds per square inch for the finer fibrous elements, which accordingly will give a harder, denser, more compact sheet. A disturbing element in the relationship between sheet density and wet fiber flexibility may be the curliness of the fibers, but this is a minor one unless the fibers were curled artificially, as will be discussed later.

It should be emphasized that, contrary to widely held opinion with an occasional dissenter,[13] fiber length *per se* is not an appreciable factor in sheet density nor air permeability; such opinions originally were based on data derived from length-fractionated whole pulps, in which experiments, as already mentioned, fiber thickness was an unconsidered covariable.

(*d*) *Fiber Cohesion*

Fiber cohesion includes both the area of fibrous elements bonded together and the intensity of the bonding. The former may be measured by optical means as developed by Parsons,[17] when the specific surface of the pulp is known. A measure of fiber cohesion as a whole is the transverse tensile strength per unit area of a test sheet. A good method for determining this is the viscosity–velocity product (VVP), measurement developed by the

[16] W. B. Campbell, Can. Dept. Interior, *Forest Service Bull.* **84** (1933).

[17] S. R. Parsons, *Paper Trade J.*, **115,** 34 (Dec. 17, 1942).

Institute of Paper Chemistry.[18] It consists in passing a heavy roller over a drop of highly viscous liquid on a face of the sheet and finding the limiting surface speed of the roller needed to blister or split the paper. The intensity of bonding may be judged by dividing the calculated force to split the sheet by the estimated percentage of the fractured area in fiber-to-fiber contact.

From a theoretical point of view, the measurement of the intensity of bonding is an interesting one, because it must relate to the chemical and physical nature of the surfaces in contact and is probably not increased by beating subsequent to the interiors of the fibers being exposed. In practice, as has already been intimated, fiber cohesion is of importance with respect to paper strength, not because of any direct resistance offered to an applied stress, which would be quite low, but because of the frictional resistance developed by individual fibers tending to be displaced lengthwise by an imposed stress. When the fibrous elements are long in relation to their diameter, as is the case with fibrils derived from cotton and bast fibers, then the magnitude of fiber cohesion becomes correspondingly less important, particularly as the sheet becomes increasingly dense and the elements are packed closer together. It must be emphasized that only relatively small cohesive forces are needed to anchor firmly a fiber embedded in a normal sheet, particularly if the fiber is long.

If the normal tensile strength of a test sheet is divided by a function, preferably the square root,[11] of the weight-average length of the fibrous elements and by the apparent density of the sheet, a practical index of fiber cohesion may be derived. This reduces cohesion to a single number which is reliable at least to the extent of telling if the pulp being tested is proficient or deficient in this property.

(*e*) *Intrinsic Strength of Fibers*

The intrinsic strength of a fiber may be found directly by attaching the ends of an individual fiber to the ends of two strips of paper with sealing wax, and measuring the tensile strength of many fibers this way by an apparatus fashioned after a chainomatic balance, then dividing the breaking load of each by its cross section measured microscopically.

Because of the delicate procedures needed to handle individual fibers and their variability which entails many data for accuracy, it is much easier to work with sheet material and determine this property indirectly by the tensile strength of the sheet as the span between jaws approaches zero as proposed by Hoffman Jacobsen.[19]

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[18] Anon., *Paper Trade J.*, **123,** 24 (Oct. 31, 1946); **123,** 24 (Nov. 7, 1946).

The assumption is made in a standard handmade test sheet that half of the fibers are oriented in the direction of pull. An improved attachment designed by Clark[20] for a tensile tester is shown in Figure 1. The test[20a] is rapid and reproducible. It can be regarded as the ultimate or maximum tensile strength of a test sheet made with the fibers being tested, after they have been subjected to a theoretically ideal beating treatment for the optimum time. The test appears to be affected by the degree of polymeri-

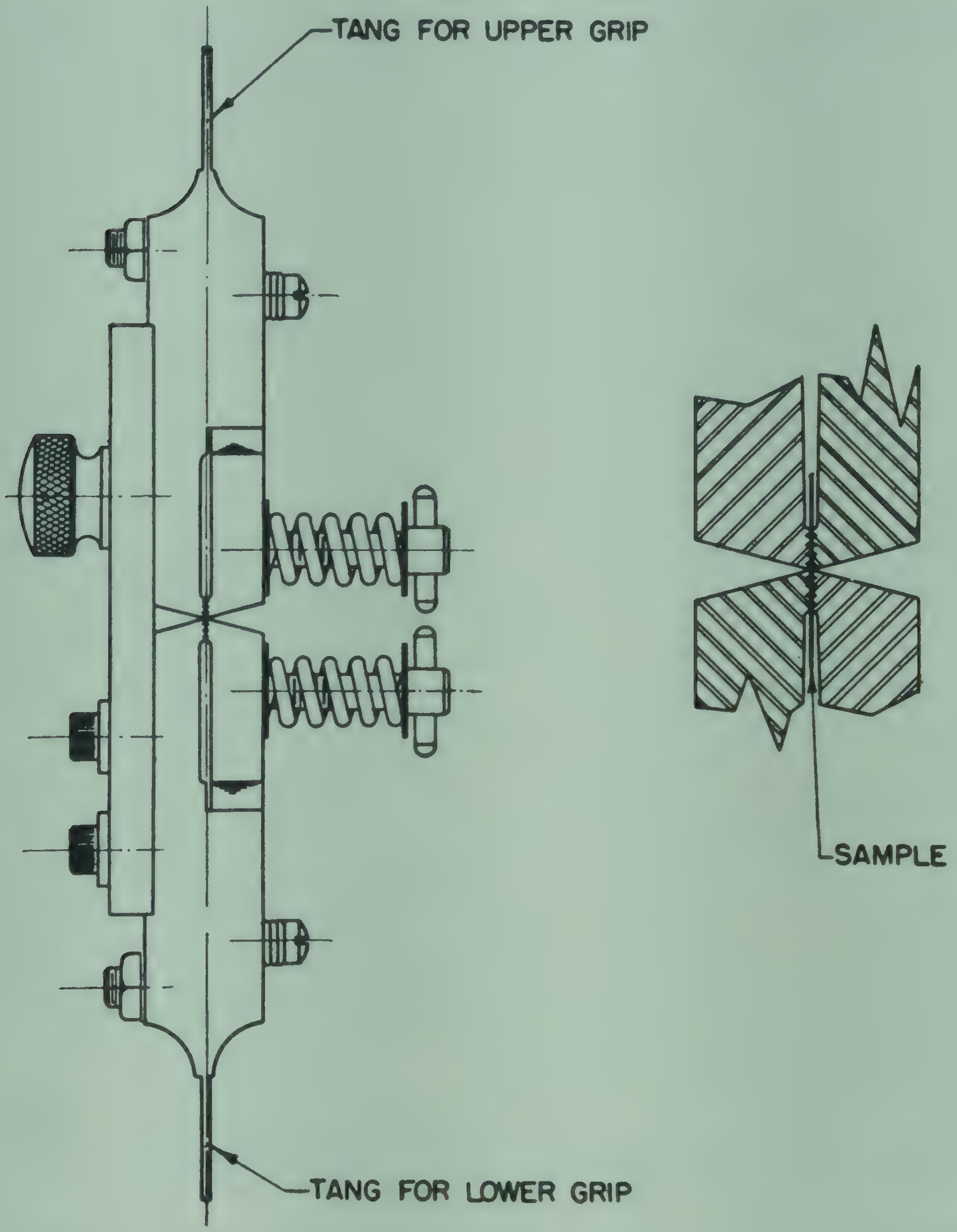

Fig. 1. Zero-span jaw attachment for tensile strength tester. Courtesy of Thwing-Albert Instrument Co., Philadelphia, Pa.

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[19] P. M. Hoffmann Jacobsen, *Paper Trade J.*, **81**, 52 (Nov. 26, 1925).

[20] J. d'A. Clark, *Paper Trade J.*, **118**, 29 (Jan. 6, 1944).

[20a] See TAPPI method T 231 sm-53.

zation of the cellulosic material in the fibers (discussed more fully under topic E-1 in this Chapter VIII) and is sensitive to overcooking or overbleaching of the pulp. As proposed by Hoffmann Jacobsen,[19] the ratio of the normal to the zero span tensile test gives a good measure of the over-all entanglement and cohesion of the fibers.

(*f*) *Pulp Evaluation and Response to Beating*

The five properties just discussed are sufficient to characterize the physical properties of a prepared or beaten pulp. Properly interpreted, they serve to forecast its "running" qualities on the paper machine (in inverse proportion to the density of the test sheets) and to predict the strength and most other qualities of the paper made from it.

Pulps differ considerably in their response to beating, depending upon the structure of the fibers and the chemical nature of their material. The measurement of beating qualities will be discussed later; however, a practical and comprehensive set of tests for evaluating the quality of an unknown pulp, including its beating characteristics, is as follows: Two portions of the sample are beaten in a standardized manner, one for a moderate time and the other for twice as long. One of these times should preferably, though not essentially, be chosen so that after that period the laboratory treatment will be approximately equivalent in extent of beating to the treatment of the pulp in practice. A set of standard pulp test sheets is made for the two beating periods. At the end of the period corresponding to the degree of beating in practice, the average fiber length, the fineness of the fibers (if unknown), the density of the test sheets, and their normal and zero-span tensile strength are measured. To serve as a check, it is desirable to apply also all the usual strength tests, such as bursting and tearing, to the sheets at that beating period. With the other beating period, only the normal tensile strength of the test sheets is needed, but it is well to measure also their density and the average length of the fibers. Provided that the two chosen degrees of beating lie on the straight part of the plot of tensile strength versus logarithm of beating, which usually will be the case, the percentage increase in the normal tensile strength of the test sheets effected by doubling the time of beating gives a good practical measure of the beating quality of the pulp.

B. BEATING

When pulp is beaten, the outstanding resulting characteristic lies in the ability of fibers so treated and thereafter dried in contact with one another, to cohere strongly. The beaten fiber mass also acquires a slimy feel and the property of holding water longer or more firmly when allowed to drain. The prepared fiber suspension, called "stuff" or "wholestuff" or "stock" is then said to be "beaten," "wet," "slow," or "hydrated." Before beating, the condition of the pulp is sometimes termed "halfstuff," but more often "unbeaten" or "raw"; after only a mild beating treatment the pulp condition is termed "free." "Wetness," "slowness," and "freeness" are derived words. These technical terms refer to the ease or difficulty with which the pulp, when squeezed in the hand or placed on a screen, either retains or parts with some of its associated water.

Beating is extremely important in its relation to the quality and the rate of production of paper. In fact, it has been said with much truth that paper is "made" in the beater. Furthermore, the interest of modern paper technologists in beating has been heightened by economic reasons. An enormous amount of power is consumed—from 200 to nearly 2000 kilowatt-hours per ton of finished paper for certain specialities although rarely is a figure of 1000 exceeded. The high cost of this one operation in papermaking is readily understood from the fact that in the United States and Canada the current annual production of paper and board is over thirty million tons.

1. Influence of Moisture on Pulp

Because of economy in transportation and also resistance to decay in a dried condition, most purchased pulps (excluding groundwood, which is not easily defibered after drying) are shipped after having been dried on steam cylinders to a dryness of over 70%, usually about 90%, in which latter condition it is technically termed "air-dry." The saturation of the fibers with water and their consequent swelling and softening is the first step in beating, although scarcely recognized as such. The rate of this swelling is somewhat dependent, inversely, on the extent to which the fibers have been dried. When swollen, they become more flexible and less brittle; because of this, they are better able to withstand cutting during the violent mechanical action of beating. Pulps which have never been dried are initially much softer and more swollen than dried fibers that have been soaked in water and, in consequence, behave differently upon being made into paper, especially after only a limited beating period. In most cases, at least one hour of mild beating treatment is required before the papermaking characteristics of a normally dried pulp revert, in part only, to those it had before being dried. This swelling of the fibers has been termed "imbibition" by some authorities and at one time was considered to be an ntegral part of the beating process itself, various vacuum and pressure devices being proposed and built into the beater to accelerate imbibition. However, except for the undisputed fact that the rubbing and squeezing of the pulp during the beating period serve to accelerate the sorption of water, imbibition is now commonly regarded as more or less incidental to beating provided that fibers are properly soaked before being subjected to intensive treatment.

2. Beating Equipment

Before considering the changes of pulps effected by beating and discussing the various theories explaining them, a brief description will be given of the principles of four types of commercial modern beating equipment. Prior to the adoption of this equipment, heavy stampers were used to break up the mass of tangled rags, commonly used as a source of fibers, into a uniform pulp.

(*a*) *Beaters, Jordans, and Refiners*

The hollander (usually termed the beater), introduced about 1670, marks the beginning of modern beating. This beater, which has changed but little in its original design, is still supreme in the fields of almost all but coarse papers and certain specialities. Figure 2 shows a cross section of a modern beater. It has the form of an oval-shaped trough A divided into two channels by a "mid-feather" B. Across the bottom of one channel, is placed the "bedplate" C which is either single or multiple; this plate is provided with projecting blades or "bars" of steel or bronze, usually from $^3/_{16}$ to $^3/_8$ in. thick and spaced about the same distance apart. These blades are set at a slight angle to the plate and project from the wooden spacers about $^1/_2$ in. Over the bedplate is mounted a heavy roll D, provided with blades or "bars" which are set parallel to the axis of the roll, which project about 2 in., and usually are spaced about 2 in. apart. The bearings supporting the roll are precisely adjustable to vary the clearance or pressure between the bars in the roll and in the bedplate. When the beater is in operation, the pulp suspension is circulated round the trough by the paddle action of the bars in the roll. Some of the fibers in the pockets between the bars are commonly supposed to be caught on the edges of the bars in the form of a "fibrage" and banged and rubbed across the bedplate bars and their edges. The pulp is discharged over the backfall E to flow round the trough to the front of the roll again. Usually the beater roll is lowered as beating proceeds and after the fibers have become sufficiently flexible to withstand a more drastic pressure without being so readily cut. The peripheral speed of the roll is approximately 2000 ft./min., the pulp circulates in the trough at the rate of about one revolution in 2 or 3 min., and the treatment is usually continued from one to a number of hours, depending on the kind of stock. The consistency of the pulp (that is, the percentage of pulp solids in a measured volume of suspension) is usually from 5 to 8%. Milne's two papers[21,22] should be consulted for further practical information on beaters and beating.

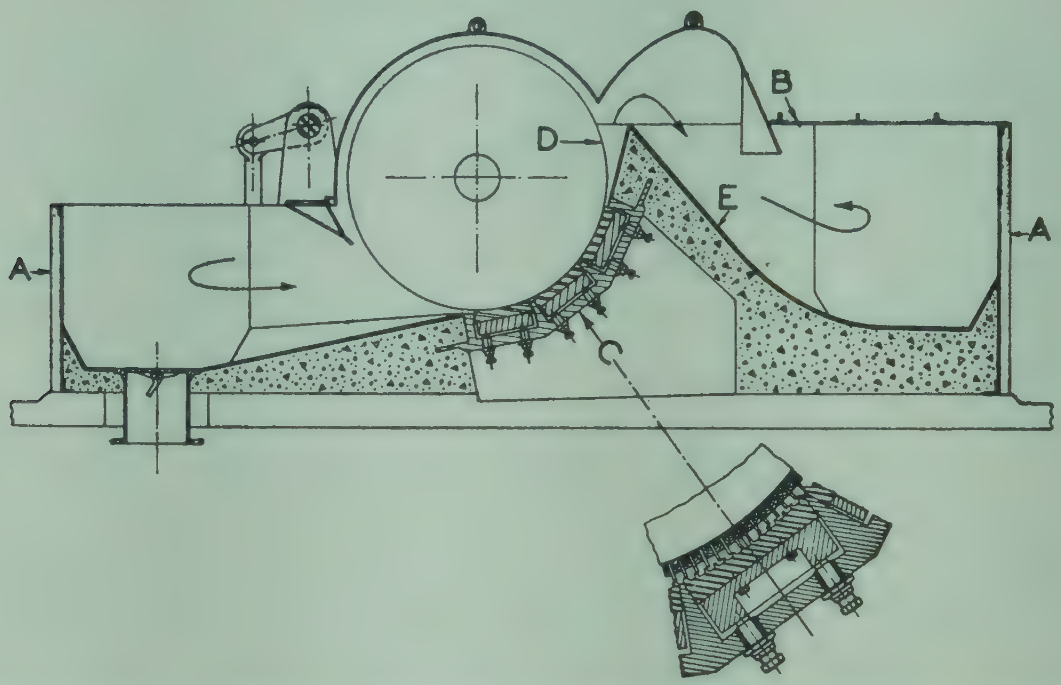

Fig. 2. Sectional view of a modern beater and detail of bedplate adjustment. (A) Beater tub; (B) midfeather; (C) bedplate (multiple shown); (D) roll; (E) backfall. The curved arrows within the diagram indicate the direction of flow of the pulp. Courtesy of E. D. Jones & Sons Co., Pittsfield, Mass.

The "jordan" has almost entirely supplanted the beater in modern mills manufacturing newsprint and kraft wrapping papers. This type of beating equipment consists of a conical drum rotating in a horizontal conical casing, the rubbing surfaces being provided with blades or "knives" similar to those described for the beater. The clearance between the knives is adjusted by sliding the drum in or out of the cone. The pulp, at a consistency between 2 and 5%, enters the casing at the small end and is moved by both pressure and centrifugal action to the exit at the large end. These machines are built in various sizes, some having a capacity for treating considerably over 50 tons of stock per day and consuming as much as 500 horsepower in so doing. In general, the action of a jordan is more that of

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[21] S. Milne, *Paper Trade J.*, **84,** 54 (June 16, 1927).

[22] S. Milne, *Pulp & Paper Mag. Can.*, **37,** No. 8 442 (1936).

cutting and especially of a "clearing" of clots and fiber bundles in contrast to that of a beater. Thus, jordans are now almost universally used on the stock for this purpose after the beaters and just prior to the paper machine.

The refiner,[23] which again is coming into favor, has found its greatest use in making kraft papers but its use is being extended to other grades. This equipment consists essentially of two large steel disks in a casing, one or both of which revolve. In a variation of this design, so as better to balance the large pressures involved, a center disk is made to revolve between two stationary ones. Like millstones, the disks have bars or serrations machined into their two adjacent faces. Pulp is fed through an opening to the center of one of the disks and passes then between the faces to the outlet on the periphery of the casing. The distance between the faces of the disks is adjustable with great precision so as to vary their action on the pulp.

More recently, a new type of refiner called an Idar has shown promise, especially for treating cotton, linters, and bast fibers. The faces of the disks of the new machine, one of which is rotated, are serrated with V grooves about $^1/_8$ in. apart to form a myriad of small sharp pyramids. The pulp is fed through into the center of the disks, where it is dewatered into clots having a high consistency. As the clots proceed outwards, presumably they are seized by the apices of the pyramids, wrenched apart, and re-formed to be wrenched apart again. In this way, a maximum of splitting and rubbing action is secured with a minimum of cutting, especially with those fibers which readily split along their lengths.

(*b*) *Special Machines*

Although the hollander, jordan, and refiner are the most widely used type of beating equipment, three other types—the rod mill, the kollergang, and the Curlator—are in limited use commercially for special purposes.

A rod mill[24] consists of a large rotating steel cylinder filled partially with heavy steel rods. The pulp, which may have a high consistency (up to 20% or more), is fed in at one end, and is subjected to the rolling and pounding action of the rods as it proceeds to the outlet at the other end. However, because of power requirements, wear of both the rods and the lining of the cylinder, and intense noisiness, very few remain in operation.

The kollergang or edge-runner[25] is used in some mills, usually paper mills, mostly in northern Europe. A typical machine consists of two heavy granite disks, about 3 ft. in diameter and 10 in. wide, mounted on horizontal axes to track around a horizontal annular trough at about 15 r.p.m. Pulp at about 30 per cent consistency is fed into the trough where it is subjected to a rolling and twisting action by the runners. Because of the very high consistency of the pulp and the manner of operation, relatively few fibers are cut. The high power consumption per ton of pulp treated and the low output per machine are reasons why, despite their desirable action, few kollergangs are used in North America.

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[23] T. W. Chambers, *Paper Making and Its Machinery*, Constable, London, 1920, pp. 50–54.

[24] S. D. Wells, *Paper Trade J.*, **111**, 89 (Aug. 29, 1940).

[25] W. Brecht, *Papier-Fabr.*, **35**, 259, 313 (1937).

A machine called a Curlator[26] has been placed in limited commercial use in the United States and Canada during the last few years. It consists of two rough-surfaced steel disks about 4 ft. in diameter, mounted horizontally one above the other. The upper disk, which bears upon the bottom disk with a pressure of about 15 lb./sq. in., is given a gyratory motion on a small radius. The action continuously dewaters and rubs the pulp fibers or fiber bundles flowing outwardly between the disks and curls the fibers. In consequence, test sheets made from the treated pulp are bulkier and thus weaker in burst and tensile strength and stronger in tear resistance and more absorbent than if made from untreated fibers.

Rod mills, kollergangs and Curlators find use mainly in pulp and paper mills making some special grades of paper. The machines are well adapted to defibering shives or slivers of wood which are incompletely softened by cooking. Their use is being extended because of a recent trent toward more "semichemical" pulping. This process entails less complete cooking of the wood chips and their subsequent reduction to fibers by mechanical treatment, usually while the material is still hot. Refiners, usually in conjunction with jordans, are also being increasingly used for the reduction of the wood chips. Pulp yields of upwards of 60% of the wood substance are attained.

3. The Action of Beating Equipment

When the bar of a beater, jordan, or refiner sweeps through the pulp, it is commonly held that a layer of fibers is caught and draped over the edge, mostly at right angles, to form a "fibrage"[27] or mat having elements lying mostly at right angles to the bar edge. This fibrage is then banged against the leading edge of one of the stationary bars, and intense pressure is developed on the assembled fibers across the zone of contact. Some of them are cut; some are split, and the tail of the outer surface of the fibrage remaining on the moving edge is rubbed across the edge and face of the stationary bar. During this action some of the fibers are transferred to the leading edge of the stationary bar and may form a secondary fibrage there. The outer face of this secondary fibrage is in turn treated by the edge and face of the following moving bar. Fibers are also rubbed against parts of the equipment and against each other as the pulp is circulated around the machine.

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[26] H. S. Hill, J. Edwards, and L. R. Beath, *Tappi*, **33**, 36 (1950).

[27] S. Smith, *The Action of the Beater*, Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland, London, 1923.

However, it is not certain that the action is as simple and as straightforward as just described. Because of the induced turbulence, there is some doubt as to the ability of the leading edge of a flat bar moving flatwise through the pulp to gather other than momentary fibrages over short lengths. If this is the case, then it is unlikely that such fibrages would be well oriented; they would be more in the nature of clots.

The predominantly pounding action of the rod mill, the rubbing and twisting action of the kollergang, and the rubbing and wrenching action of the Idar have been mentioned. These do not preclude cutting and splitting the fibers, since, when two or more wet fibers cross each other and are compressed between two hard surfaces, mutual cutting of the fibers can and does occur.

On a greatly magnified scale, the beating operation would be analogous to pouring bushel baskets of very long cigars between two trains passing each other at high speed with a clearance between them of only a couple of inches. Under this action, the cigars would be cut, or would cut each other; they would be split externally, unravelled, and rubbed. Much of the "wrapper" would be loosened and removed and the inner filler would be split, separated, and bruised. Some cigars would be bent, and a large amount of tobacco dust and small pieces would also result. In all beating operations, it will be clear that fibers are cut, split, bruised, and, usually to a minor extent, bent or curled. Fiber debris is always produced, and new surfaces are opened up and exposed to water which is immediately adsorbed. Accordingly, the beating action given to fibers by any piece of beating equipment may be characterized and measured in terms of (1) cutting (shortening), (2) splitting, which in turn may be subdivided into (a) surface splitting or roughening—as a result of rubbing, and (b) internal splitting—as a result of bruising, and (3) deformation or curling of the fiber—usually negligible unless the fibers have been treated with a Curlator or in a commercial kollergang at high consistency. It should be emphasized that these three basic actions, together with the adsorption of water on exposed cellulosic surfaces, are the only things that can possibly happen during beating. The so-called "hydrating" action of the beater is presumed to be equivalent to the splitting of portions of the exterior and interior of fibers and the sorption of water on the newly exposed surfaces.

The over-all and relative extent of the three basic actions on a given pulp will depend on the design of the equipment, the manner of its operation, and the consistency of the pulp being treated; temperature has a small, usually negligible, effect. For a given pulp, cutting of the fibers will be promoted relative to the other actions by the following: (a) Low pulp consistency—Thinner fibrages or clots will be formed on the bar edges so there will be less cushioning at impact and more intensive pressure. (b) Bar sharpness—There is much erosion and corrosion of the bar edges in beating equipment. New bars cut more than worn ones, thin ones more than thick, and, despite contrary statements in the literature, relatively soft noncorroding metal bars like bronze or monel often cut more than do steel bars, especially hard steel bars, which do not wear away nearly as fast as their leading edges become rounded. (c) Bar angle—It has been held that the less parallel are the fixed and moving bars, the greater is the scissoring or cutting action. However, unless the bars are very sharp it is very doubtful if this is much of a factor. (d) Bar speed—For a given applied horsepower, a lower speed means a lesser clearance between the bars and consequently a greater cutting action. On the other hand, fibers, especially when wet, are capable of extensive plastic deformation, so that, if, during beating, cutting forces are applied more suddenly, increased bar speed, especially beyond about 2500 feet per minute, favors relatively more cutting. However, as pointed out by Rance,[28] there is an analogy between the mechanism of oil lubricating a bearing and the pulp suspension acting as a lubricant between the fixed and moving bars. Thus an increase in the speed of the moving bars may sweep more fibers into the zone of action and to that extent reduces the tendency for cutting to occur. (e) Rigidity—The firmness and inertia of the bars and bar-holding parts intensify the imparted shock, which, for the reason just discussed, favors relatively increased cutting. Accordingly, in general, mill equipment will do considerably more cutting and smashing of fibers to produce debris than will laboratory equipment, even if other factors are substantially the same. (f) Bar clearance or pressure—This is the main adjustable variable for control purposes and governs the power input to the beating machine.

Internal splitting depends on the nature of the fibers, but will be increased by high consistency of the pulp, blunt bars, and medium bar pressure. Surface splitting or rubbing is favored by high consistency, high bar speed, and low bar pressure. If a "stone" bedplate and a "stone" roll, actually made of basalt lava, the roll having wide, deep channels cut across its face like a broad gear wheel, are substituted for the usual beater roll with metal blades, or if the bedplate is made of stone and the roll of metal, the rubbing and bruising action of the beater will be intensified. Accordingly, such equipment is especially desirable for greaseproof papers and some specialties, such as ultrathin electrical condenser tissues, but unfortunately the lower output and thus higher power consumption per ton of stock prepared with stone tackle are considerable disadvantages.

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[28] H. F. Rance, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **32,** 360 (1951).

It is almost axiomatic that the more power that can be applied to any given beating machine working on pulp, the less power per ton is needed to beat the pulp. This is so because, in general, a substantial portion of the applied power is largely wasted in circulating the mass of pulp and water, and the power loss for this does not increase as the total applied power is increased. However, unless the consistency of the pulp can be raised to offset the increased bar pressure involved, the quality of the prepared stock is then likely to suffer to some degree.

4. Measurement of Beating

The effects of beating which have been most used for its measurement have been (1) reduction in fiber length, (2) difficulty in draining water from a mass of pulp, (3) increase in the density of test sheets, (4) increase in the specific surface of the pulp, and, as already discussed, (5) increase in the tensile strength of test sheets.

The oldest and most straightforward method of judging the degree of beating is the estimation of the length of the fibers, originally by direct inspection, more recently with a magnifier or by optical projection. By modifying the operation of a high-speed fiber classifier,[15] the percentage of fibers longer than a chosen length may be determined in a few minutes; it is possible, therefore, that this method will again take the leading place.

Since the beginning of this century, scores of tests and instruments became available for measuring the rate at which "free" or "fast" water drains from pulp. These tests are empirical and are conducted under specified conditions. Results are usually reported as (a) drainage time, that is, the time required to form sheets of a certain moisture-free basis weight (TAPPI Standard T 221 m-51), or as (b) the "freeness," that is, the volume of "fast" water drained from the pulp (TAPPI Standard T 227 m-50).

Unfortunately, the freeness test is affected by many different factors, particularly the quantity of fine debris present in the pulp. In fact the "freeness" of a well-beaten pulp can be almost fully restored to its original value by washing beaten pulp with water on a 200-mesh sieve and so removing the debris without greatly affecting the strength.[8] In consequence, because of the highly questionable, and indeed erroneous, implicit assumption that the quantity of fine debris produced by all kinds and sizes of beaters and other machines is proportional to their beating action, whereas it may vary greatly even with a single laboratory beater, the custom of reporting the strength or other properties of pulps beaten to a given freeness is always indefinite and often misleading.

Clark[8,29] has found that when the apparent density of the test sheets, or better still its inverse, the apparent specific volume, is plotted vs. logarithm of either the amount of energy supplied or the beating time, if the energy supplied per pound of pulp is constant, the resulting plot is a straight line. This may except the initial point for unbeaten pulp which is sometimes disturbed in position by the presence and quick removal of the primary wall, and will except the final points if the pulp is beaten considerably beyond the normal commercial limit. It was also found[8] that the slopes of the lines so plotted for a wide variety of pulps treated with the same beater and under the same conditions are surprisingly parallel. Thus, the plot for a straw pulp gives a slope similar to a wood pulp or a rag pulp but commences at a lower specific volume—about 1.5 instead of about 2 and 2.5 cc./gram, respectively. These findings make the specific volume of the test sheets (or their density) a most useful basis for measuring the degree of beating. A minor drawback to using either the density or specific volume is their comparative insensitivity and consequently the time and care needed to make a measurement with sufficient precision. The longitudinal shrinkage of the test sheets before and after drying is an analogous test which is more sensitive and may serve for control purposes when suitable equipment for determining density, such as that described in TAPPI Standard T 205 m-50, or adequate time, is not available.

The specific surface of a pulp (see TAPPI method T 226 sm-52) appears to increase linearly with the logarithm of the amount of beating, at least during the initial and intermediate stages and at a different rate with different pulps. It would make an excellent measure of beating if it were not so difficult to determine reliably.

When the tensile strength or its function, breaking length, is plotted against the logarithm of the amount of beating, the result is linear over

[29] J. d'A. Clark, *Paper Trade J.*, 116, 31 (Jan. 7, 1943).

most of the practical range of beating and the slope varies with different kinds of pulps. When the slope of this line is determined with standardized reproducible laboratory beating equipment as discussed in Section A-3-f of this Chapter VIII, it constitutes possibly the best current practical measure of the beating quality of a pulp.

C. THEORIES OF BEATING

Because of its importance, beating has been the subject of many published articles and discussions, but even yet there is not complete unanimity concerning the cellulose-water relationship in beating.

In order to explain the various known effects of beating, hypotheses have been offered which may be divided into two main groups: chemical and physical, with the colloidal aspects of the latter receiving increasing support. Associated with these differing views, respectively, are the names of Carl Schwalbe,[30] James Strachan,[31–33] and W. Boyd Campbell,[16,34] whose main theses may be found in the references noted. Also among the more comprehensive papers on the subject are those of Bell,[35,36] Cottrall,[37,38] Harrison,[39] Kress and Bialkowsky,[40] and Jayme[41] and extended treatments of special phases of the problem by Katz[42] and especially Stamm,[43] and the reviews of the subject by Simmonds,[44] Rowland,[45] Clark,[46] and Sutermeister.[47]

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[30] C. G. Schwalbe, *Paper Trade J.*, **72**, 58 (Mar. 3, 1921).

[31] J. Strachan, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **6**, 139 (1926).

[32] J. Strachan, *ibid.*, **13**, 61 (1932); **14**, 447 (1933).

[33] J. Strachan, *ibid.*, **19**, 171 (1938).

[34] W. B. Campbell, *Paper Trade J.*, **100**, 35 (Feb. 14, 1935).

[35] J. H. B. Bell, *J. Soc. Chem. Ind.*, **52**, 109T, 119T (1933).

[36] J. H. B. Bell, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **15**, 401 (1934).

[37] L. G. Cottrall, *ibid.*, **14**, 241 (1933).

[38] L. G. Cottrall, *Tappi*, **33**, 471 (1950). See especially L. G. Cottrall, *Introduction to Stuff Preparation for Papermaking*, Griffin, London, 1952.

[39] H. A. Harrison, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **11**, 303 (1930).

[40] O. Kress and H. Bialkowsky, *Paper Trade J.*, **93**, 35 (Nov. 12, 1931).

[41] G. Jayme, *Australian Pulp & Paper Ind., Tech. Assoc. Proc.*, **3**, 432 (1949).

[42] J. R. Katz, *Cellulosechemie*, **11**, 17 (1930).

[43] A. J. Stamm, U. S. Dept. Agr., *Misc. Pub.* **240** (1936).

[44] F. A. Simmonds, *Paper Trade J.*, **101**, 35 (July 18, 1935).

[45] B. W. Rowland, *Paper Trade J.*, **101**, 98 (Sept. 26, 1935).

[46] J. d'A. Clark, *Paper Trade J.*, **97**, 25 (Dec. 28, 1933).

[47] E. Sutermeister, *Paper Ind. and Paper World*, **29**, 361, 542 (1947).

1. Chemical Theory of Beating

The chemical theory of beating, which was held by such prominent investigators as Cross and Bevan,[48] Sindall,[49] and later championed especially by Schwalbe,[30] suggested that during beating, the fibers were cut and fibrillated and at the same time a cellulose hydrate or slime, which was presumed to be a chemical compound of cellulose and water, was formed round the particles and provided a strong adhesive which, when dried, cemented the structure together. Cross and Bevan were somewhat noncommittal about whether or not a true cellulose hydrate was formed, and chose to term it "physicochemical" combination, but both Schwalbe and Sindall found experimentally that beaten pulp was slightly more hygroscopic than unbeaten pulp and, accordingly, believed that some hydrate was formed. Subsequently, very precise measurements[16,50] of the equilibrium moisture content of the same pulps, both beaten and unbeaten, have disclosed that the former usually, but not always, do contain more moisture, that is, up to 4% of the total moisture present. However, because of no definite experimental evidence as to the presence of a hydrate, the slight excess of moisture in the beaten pulps may be very satisfactorily explained on the basis that intensive beating has opened up the internal structure of the fibers and provided fresh surfaces to adsorb additional moisture.

Some investigators have suggested, on purely hypothetical grounds, that a liquid mucilage of carbohydrate material is formed in greater or lesser quantities when water permeates a fiber and this is squeezed to the surface when the fiber is subjected to mechanical treatment. Wurz,[51] for example, has postulated that pectin-like substances, uronic acids, are a necessary content of pulps from which well-bound papers like greaseproof can be satisfactorily made.

The chemical theory of beating was a very comfortable one to the papermaker as it could be made to explain satisfactorily almost, if not quite all, the more practical beating phenomena which have been referred to above. In particular, by the apparently reasonable postulation that the hydrate was glue-like in character and increased in quantity as beating proceeded, a good explanation was provided for the characteristic way in which the strength of sheets made from cellulose fibers increased with beating. Indeed, Schwalbe[52] not only proposed the use of chemical agents, such as acids and alkalies, to expedite beating by the formation of a hydrate, but he even carried out one or two apparently satisfactory commercial demonstrations.

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[48] C. F. Cross and E. J. Bevan, *A Text Book of Papermaking*, 5th ed., Spon, London, 1920, especially Chapter VII.

[49] R. W. Sindall, *The Manufacture of Paper*, Constable, London, 1908, especially Chapter IX.

[50] S. E. Sheppard and P. T. Newsome, *Ind. Eng. Chem.*, **26**, 285 (1934).

[51] O. Wurz, *Papier-Fabr.*, **35**, Tech.-wiss. Tl., 54, 57 (1937); **38**, Tech.-wiss. Tl., 87 (1940).

2. Physical Theories of Beating

The main difficulty in securing a general acceptance of any one physical theory, on the other hand, has been the absence of an equally satisfactory and simple explanation of the mechanism of bonding as was provided in the chemical theory or by the mucilage or glue hypothesis; it is with this point especially that many investigations and differences of opinion have been concerned.

The chemical theory was severely criticized by Strachan in 1926.[31] He insisted that the taking up of water by pulp in beating should be termed "imbibition" and not hydration. He described the water content of paper stock as follows: (1) water of suspension, in which the fibers float; (2) capillary water held between the fibers and in their canals and pores; (3) colloidal water composed of (a) water of "imbibition" adsorbed by the unbeaten fiber and (b) water of "hydration" or an increase of water of imbibition due to beating. The colloidal water was stated to be held partly by adsorption and partly by occlusion.

Strachan described a number of experiments which he conducted on artificially made fibers having a density of 1.2, prepared from rag paper moistened with zinc chloride and compressed together followed by thorough washing ("vulcanized" fiber), and demonstrated quantitatively the effects of vacuum, pressure, temperature, papermaker's alum, acids, and alkalies on the rate of imbibition of his material, which was presumed to be analogous to the fiber of a pulp.

(a) *Fibrillar Entanglement*

After describing his concept of the internal structure of the cellulose fiber, confirmed later by others,[53,54] Strachan postulated that the layers of compacted fibrils, being porous, allow water to penetrate and thus cause the fiber to swell. When the fiber is then subjected to the beating action, the outer layers are loosened, and the surface becomes fibrillated, there is easier access of the water to the inner layers, and the rate of water penetration is thus increased. He considered that beating increases the water content of the fibers by the dual effects of fibrillation, which enables the fibers to hold more water, and by the pressure to which the fiber is subjected. For example, increasing the consistency of pulp in a beater results in a greater effective pressure being applied and, consequently, faster "hydration" or increase in imbibition. He pointed out that only the surface of the fibers is affected by prolonged light beating, and under these conditions a strong opaque paper, such as currency paper, is obtained; whereas, if the fibers are subjected to intensive beating, the whole mass is bruised and softened and fibrillation takes place throughout the fibers, giving a more transparent, greaseproof type of paper. When a sheet of paper is made, the fibers of beaten stock are soft and fibrillated and lie and adhere together more closely than unbeaten fibers on the forming wire of the paper machine. Between the press rolls, the fibers are squeezed and are drawn in intimate contact according to their degree of plasticity and degree of fibrillation. As the fibers are dried, the water of imbibition is forced out and they shrink. The outer layers of the fibrils on the fibers also shrink together, so that the dried fibers become coated with a layer of denser structure than was previously the case. The fibers are no longer as porous as they were before beating, because the air spaces have been largely closed, producing hardness and transparency in the mass. The compacting of and cohesion between the fibers, finally, is somewhat increased by the subsequent calendering. During the process of beating, some of the fibrils become detached from the fiber; Strachan held such material to be useless from the papermaking viewpoint. He assumed cohesion between the fibers to be caused primarily by the mutual entanglement of the fibrils produced by beating, the detailed mechanism involved being described merely by a statement that it is in accordance with "well-known physical laws."

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[52] C. G. Schwalbe, *Paper Trade J.*, **80**, 46 (Jan. 22, 1925).

[53] G. J. Ritter and G. H. Chidester, *Paper Trade J.*, **87**, 131 (Oct. 25, 1928).

[54] G. W. Scarth and J. D. Spier, *Trans. Roy. Soc. Can.*, **23**, 281 (1929).

Strachan's explanation of the beating action was held by several critics[55] to be incomplete in a number of particulars. Some exception was taken to his denial of the existence of a true cellulose hydrate, such as has already been discussed, but more important was the fact that his theory did not explain the marked increase in strength obtained in paper made from pulp which was given only a mechanical stirring treatment in water, even though previously the pulp was thoroughly soaked. Strachan, however, claimed that even with such a slight treatment, an exceedingly fine degree of fibrillation, which was sufficient to account for the increased strength, actually occurred.

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[55] Discussion, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland,* 13, 1 (1932).

The work of Kress and Bialkowsky[40] confirmed the opinion that no appreciable chemical changes occurred with beating except an increase in the sensitiveness of the pulp to hydrolysis and a slight decrease in the cuprammonium viscosity, effects which may be ascribed to mechanical changes. They noted that a beaten pulp sorbs no more methylene blue dye from an aqueous solution than does an unbeaten pulp. Although methylene blue is positively charged in solution, it appears to be able to penetrate the intermicellar structure of the cellulose quite easily.

This finding was later confirmed by Strachan[33] and was held by him to prove that the total (i. e., including the internal) specific surface of the cellulose was not increased by beating. Strachan[32] also showed that the retention of positively charged sols like silver oxide, especially when precipitated in the presence of pulp, increased markedly as beating progressed, which indicated an increase in the external specific surface.

Kress and Bialkowsky[40] furthermore reported the results of a number of experiments with pulp and various organic liquids. They measured the swelling action of the different liquids on cellulose and found that the swelling power corresponded with the degree of beating obtained and with the strength developed in the resulting paper when cellulose was beaten in that liquid. No strength or swelling was developed in oil, very little in alcohol, considerable in ethylene glycol and in water, and still slightly more in formamide. No visible fibrillation was developed in oil or alcohol even after intensive beating. They conclude that "these physical changes are mainly occasioned by the swelling of the fibers by the liquid in which the stock is beaten, with the result that there is an increase in the volume of the fibers. In the wet swollen condition, the fibers are low in strength but are highly plastic and ductile, and any mechanical action will tend to bruise and fibrillate the fibers rather than to produce a sharp cutting action. The hard close nature of the paper made from so-called hydrated stock seems to be due entirely to the fibrillation of the fibers and the shrinkage of the fibers when the liquid producing the swelling and shrinking is removed by drying." It will be noted that this conclusion is in accord with that previously reached by Strachan.

(*b*) *Partial Solubility of Cellulose*

A different view of the mechanism of bonding was presented by Campbell[56] in 1932, and most of the subject matter in this and some later articles on the subject were published in 1933 in pamphlet form.[16]

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[56] W. B. Campbell, *Paper Trade J.*, **95,** 29 (Oct. 25, 1932).

A few years previously, Urquhart[57] had advanced the hypothesis that, during the formation of cellulose in nature, a precipitate was formed in the presence of water and, hence, the hydroxyl groups would have molecules of water attached. As the fiber dried, the hydroxyl groups would be freed from water and their residual valences would be extensively satisfied by those of adjacent cellulose molecules. When the fibers were again wetted with water, some of these bonds would be broken and some of the hydroxyl groups would reattach themselves to water, giving a looser form of structure. If this water is driven off again, the groups once more mutually bind together. This concept was accepted and extended by Campbell who suggested that, because of their "partial solubility," the molecules, especially the short-chain molecules, when exposed on the surface of a fiber by beating, were on the verge of solution. They were thus endowed with a freedom that enabled the molecules of adjacent fibers to so orient themselves that, upon drying, many of their hydroxyl groups could bind together by means of secondary valence forces.

In connection with "partial solubility," Wislicenus and Gierisch[58] found that, after breaking down pure cellulose fibers by very fine dry grinding, up to 0.4% of the resulting powder became soluble in water and, because the amount of ash in the dissolved portion was little more than in the original paper, it was clear that part of the cellulose itself had dissolved; chemical tests indicated that the dissolved material had undergone considerable degradation. Strachan published data to show that appreciable (though very small) quantities of material, from 13 to 21 parts per million, were dissolved by cold water from a carefully purified cotton cellulose, even after as many as fifty extractions. Upon evaporation, the hydrolyzed residue had a reducing action equivalent to about 15% of its weight of glucose. Also, in a discussion of Strachan's paper, Turner[59] described experiments he had carried out by dipping a highly purified cotton fabric in conductivity water. The brown line formed where the water evaporated consisted of material which was soluble in alcohol and which possessed considerable reducing power. The line could be re-formed at lower and lower levels on the same piece of cloth with undiminished intensity, which indicated that, by some chemical change, the cellulose was being transformed into a water-soluble material.

There thus exists some indirect experimental support for the idea of "partial

[57] A. R. Urquhart, *J. Textile Inst.*, **20,** T125 (1929).

[58] H. Wislicenus and W. Gierisch, *Kolloid-Z.*, **34,** 169 (1924).

[59] H. A. Turner, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **19,** 182 (1938).

solubility" of the cellulose surfaces in water as expressed by Campbell and for the concept that some of the molecules on the surface are on the verge of, or are even completely in, solution, especially those molecules of cellulose and allied materials having a relatively short chain length. Furthermore, it has been shown that a completely acetylated pulp has little strength if made in water but has considerable strength if formed in alcohol or acetone in which it is partially soluble.[50] Also, partial methylation[61] or partial acetylation[60,62] under carefully controlled conditions appreciably increases the strength of paper formed from the pulp.

Clark[63] has ventured an opinion that essentially the primary hydroxyl groups are involved in the linkages holding the cellulose chains together. This structure cannot readily be broken by water, but if these linkages are disturbed by the primary hydroxyl groups becoming either loosely engaged with cuprammonium complexes or xanthates or by being converted to carbonyl, ester, or ether groups, the material becomes much more hygroscopic and even soluble in water, provided that most of the secondary hydroxyl groups are left substantially intact and are not transformed to hydrophobic radicals. This, statistically at least, appears probable during the early stages of conversion of the cellulose to a derivative.

(c) *The Mechanism of Bonding*

Campbell[16] also showed by calculations that, especially with the finer fibrils, as the water is removed the normal surface tension forces, which with pure water amount to about 2 × 70, or 140 dynes per centimeter of filament irrespective of diameter, give rise to enormous compacting pressures, which further increase the surface areas in contact. This explains why well-beaten stock compacts so easily on drying, giving a hard, dense, strong paper. That this is the mechanism responsible appears to have been confirmed by Van den Akker.[64] He showed that if an undried pulp test sheet was frozen and the water removed by sublimation in a freezer, the resulting dry sheet was bulky, opaque, fluffy, and weak.

Campbell concluded that, when fibers have access to moisture, a layer of water is adsorbed on every exposed crystal surface and a layer of hydrated cellulose (in a colloidal sense) is thus produced. The association of the

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[60] J. C. Bletzinger, *Ind. Eng. Chem.*, **35,** 474 (1943).

[61] G. Jayme and D. Froundjian, *Cellulosechemie*, **18,** 9 (1940).

[62] W. H. Aiken, *Ind. Eng. Chem.*, **35,** 1206 (1943).

[63] J d'A. Clark, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **24,** 30 (1943); *Paper Ind. and Paper World*, **25,** 382, 507 (1943).

[64] J. A. Van den Akker, *Tappi*, **35,** 13 (1952).

hydroxyl groups with water lowers the attraction of the crystallites for each other along the natural crevices and cleavage planes in the fiber, the interior of which, it will be recognized, is normally under tension from having been dried, so that small passages are split open and additional water enters, resulting in further adsorption and swelling. Beating bends and stresses the swollen and softened structure, and the fiber becomes still more flexible. Fibrillation also occurs, greatly increasing the external surface of the fibers. When the fibers are made into paper and the water is removed, the extent of bonding depends on the flexibility of the fibers and the amount of surface exposed, both being clearly dependent upon the degree of beating. The degree of orientation of the crystallites in contact with each other, which also depends somewhat on flexibility, is an important factor in the degree of bonding; thus, if the crystallites happen to be parallel and point the same way when they come together, the degree of bonding will be at its maximum.

In practice, there is a range of bonding from the slight bonding shown in blotting paper (which is both weak and opaque) to the extreme case of glassine paper where the transparency, degree of bonding, and water insolubility of the bonds are at a maximum for paper.

This explanation of the process of bonding, akin to the phenomenon of crystallization, was at variance with the conclusions of Strachan,[32] who took exception to it on the ground that the union of crystal surfaces demanded that the surface must be either malleable or liquid (e. g., dissolved), so that the crystal surfaces could be oriented similarly. He stated[33] that the first condition was obtained to a limited extent in the parchmentizing process (of vegetable parchment) and the second in the case of making cellophane, but neither condition was fulfilled with cellulose under normal papermaking treatments. He re-emphasized his opinion that "during beating, the surfaces of the fibers are rendered plastic by fibrillation. The fibrils of the two beaten surfaces become entwined and bind together. We have not only intertwining of the fibers themselves, but also intertwining of minute fibrils.... As the external surface of the fibers increases with beating, so the cohesion between such surfaces increases in the presence of water which brings them into contact."

However, Strachan's grounds for insisting upon that mechanism of bonding exclusively, disappeared when Clark[46] published his findings of the surprising shear strength developed by the bond formed when two sheets of normal uncoated cellophane, which certainly were not fibrillated, are wetted, cleaned, then pressed and dried together. He also showed that molecular orientation, as Campbell had suggested, played an important part in their cohesion.

Harrison, in the course of several contributions as a result of many careful experiments on beating,[39] published[55] some photomicrographs showing mildly beaten fibers apparently devoid of fibrillation which nevertheless formed quite strong sheets of paper and concluded accordingly that fibrillation was not alone responsible for strength. Indeed, he pointed out that when fibrillation became pronounced after much beating, the rate of strength development was then barely increasing. Cottrall[38] published other photomicrographs later which appear to support the same viewpoint. In his recent book,[38] an interesting theoretical and practical review of beating and refining, Cottrall continues to minimize the importance of external fibrillation and instead emphasizes wet fiber pliability enhanced by the presence of hemicelluloses and internal fibrillation brought about by beating

Edge[65] showed that, when coarse fibrillation was developed by beating a pulp in toluene, if the toluene was then displaced by water and sheets were formed, only a small fraction of the normal strength was obtained as compared with both beating the pulp and forming the sheets in water.

Bell[35] gave an account of an extensive series of experiments dealing with the drainage, shrinkage, and properties of masses or cakes of beaten and unbeaten pulps and several liquids, together with a discussion of beating on the basis of chemical, colloidal, and physical properties of the fibers. In this and in a later paper[36] where the question of cohesion is further discussed, he concluded: "Sheet strength must be due to a loose chemical bonding between the fibers...and is probably effected through the free hydroxyl linkages in the outer transverse surfaces of the cellulose micelles... Beating exposes...a greater external surface with its quota of free hydroxyl groups. If, however, we can obtain sheet strength without much fibrillation, there must be some other way of liberating these hydroxyl linkages during beating." He then suggested that the actual existence of the Lüdtke[66] noncellulosic membrane system, enclosing the fiber elements, and its rupture, would account for this, and was inclined to think that fibrillation played a subordinate part.

(*d*) *The Surface of Fibers*

It will be noticed that, with the possible exception of the mucilage-formation hypothesis which so far has no valid experimental basis, none of these physical theories accounts satisfactorily for the considerable rate of increase of strength always noticed during the preliminary stages of beating.

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[65] S. R. H. Edge, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland,* **16,** 273 (1935).

[66] M. Lüdtke, *Cellulosechemie,* **13,** 169, 191 (1932); **14,** 1 (1933).

To investigate the problem further, Clark[67] devised a method for depositing a fine film of metallic silver on wet cellulose fibers. This permitted measurements of the specific surface of beaten and unbeaten pulps to be made with a reasonable degree of accuracy (TAPPI method T 226 sm-52). In addition, the finer structure of beaten fibers, including the ultra-fine fibrils described by Strachan, could be then observed with ease. The silvering step may be recommended as an excellent morphological stain for the microscopy of cellulose, since many normally invisible details thereby become resolved. The colors vary from pale yellow through a range to dark brown and black.

Figure 3 shows an interesting microphotograph of two bleached sulfite fibers from a sample of pulp which was subjected to rapid stirring only, at 3% consistency for about 100 minutes, corresponding to a very mild beating treatment. A thin film of silver was then deposited on the fibers, just thick enough to cover the surfaces and make the very fine fibrils visible; this also revealed the structural details of the loosened primary wall material which, because of its thinness, is very difficult to see under usual conditions. This sheath, which apparently has less reducing power than the body of the fiber at this initial stage of silvering, is colored a golden yellow by transmitted light, whereas any fibrils on the secondary walls are almost opaque. Impressions of the bordered pits may be seen on the loosened sheath on one of the fibers in Figure 3. Where the sheath is still on the fiber or where it is folded over itself, there is no trace of fibrils or fuzz on its surface; on the other fiber, the skin of which apparently has been rubbed off, there is a uniform covering of very fine fuzz. Without the silvering operation, which requires a high degree of skill, this fuzz is exceedingly difficult to resolve and requires a microscope with a high numerical aperture and critical illumination. The presence of the fine fuzz on the body of the fiber and its absence on the outer sheath have since been confirmed with the electron microscope. It is this fuzz which Strachan maintained was present on lightly beaten fibers. In this connection neither he nor others had previously described the functions of the primary wall or outer sheath before or after beating, the freedom of the surface of the fibers from fuzz or fibrils prior to its removal, and the subsequent automatic appearance of the very fine fibrils on the secondary wall beneath.

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[67] J. d'A. Clark, *Paper Trade J.*, **115**, 32 (July 2, 1942).

There has been some confusion in the literature between the identities of the primary wall and the outer layer of the secondary wall. Wardrop and Dadswell[68] have recently given a clear summary and account of the matter with photomicrographs of the structure. It may be mentioned that the constrictive spiral windings observed on solvent-swollen wood pulp fibers that have not been overcooked or overbeaten are derived not

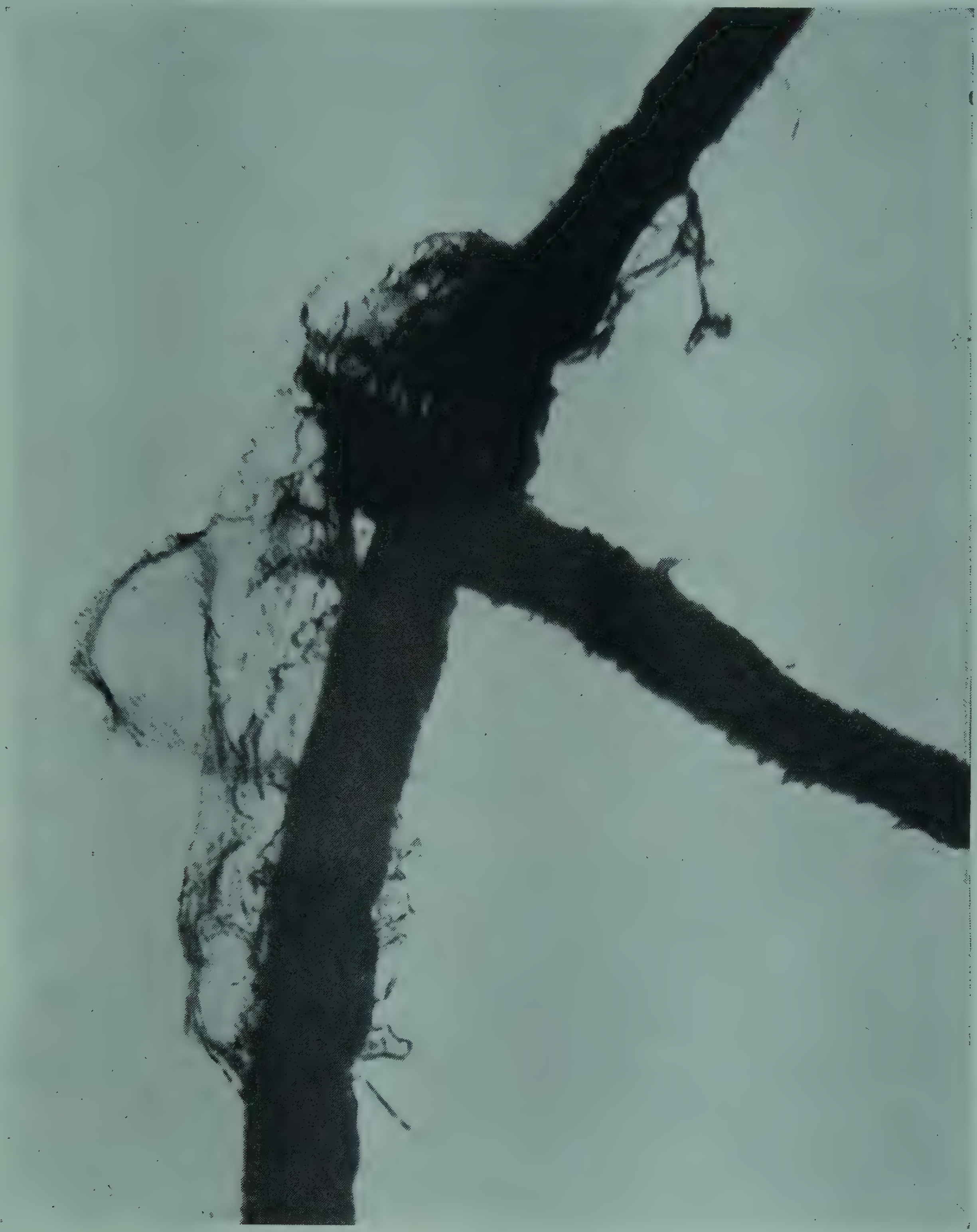

Fig. 3. Portions of two bleached sulfite fibers from western hemlock after long stirring and after being lightly silvered (Clark[67]).

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[68] A. B. Wardrop and H. E. Dadswell, *Australian Pulp & Paper Ind., Tech. Assoc. Proc.*, **4**, 198 (1950); **5**, 204 (1951); *Holzforschung*, **7**, 33 (1953) (in English).

solely from the primary wall but from the outer layer of the secondary wall, which is a well-oriented, strong, crystalline, fibrous cellulose structure. On the other hand, the primary wall is usually a weak, somewhat brittle membrane, which, as Wise and others[69] have recently indicated, appears to consist largely of mannans. It is probably incapable of causing the observed constrictions and is incapable of fibrillating although, of course, it may be shredded.

By relating the action of a known weight of silvered fiber in the catalytic decomposition of a standardized dilute solution of hydrogen peroxide with the action of a measured area of small shreds of cellophane sheeting also silvered, it was found, as mentioned, that the external specific surface of the pulp increased in proportion to the logarithm of the amount of beating, that is, very rapidly in the initial stages of beating, corresponding closely with the rapid increase in the strength of the resulting papers in those early stages. Notwithstanding the mildness of the treatment to the fibers shown in Figure 3, their specific surface was 36% higher, and the tensile strength of sheets made from them 270% higher, than the pulp before treatment.

3. Composite Theory of Beating

Considering these later observations with others, especially those of Strachan, Campbell, and Bell, the following modified theory of beating was formulated by Clark.[63]

During the chemical and mechanical treatments involved in the preparation of pulp, the primary wall of the fiber, which is permeable to but is not swollen by water, is partially cracked, rubbed loose, or removed to expose some of the underlying surface of the fiber. In the case of wood pulps, this underlying surface is the spirally wound outer layer of the secondary wall.

When water enters the interior of the secondary wall (body of the fiber) the fiber commences to swell to almost the original size it had in the living plant because the water penetrates the voids between the micelles and breaks a number of bonds holding the structure tightly together, possibly those between the secondary hydroxyl groups by combination and those involving the primary hydroxyl groups by the splitting action of the elements as the fibers swell.

The rubbing and the partial solvent action of the water almost immediately form a kind of two-dimensional colloidal suspension of the cellulose and other carbohydrate material on the exposed and interior wetted surfaces in the amorphous regions of the secondary wall. The "concentration" of the "suspension" is believed to be dependent inversely on the degree of polymerization of the cellulose and allied material that is exposed. This state is regarded as a colloidal system in which the particles are fixed or anchored at one end but otherwise subject to all the usual laws of colloidal behavior. The surfaces of these particles, bearing hydroxyl groups, are strongly hydrophilic and attract and bind a number of consecutive layers of water molecules which, especially near the solid surfaces, are well oriented and closely packed.[70] It is this water envelope that is the so-called "water of hydration" and that gives rise to the various phenomena associated with it. The molecules of water adjacent to the cellulose surfaces are probably held by hydrogen bonding to the hydroxyl groups; if a hydrogen bond is regarded as a chemical bond, then this portion of the water may be regarded as being chemically bound. The primary wall is not in any way water soluble, and in fact Brauns and Lewis[71] found that the material from the outer surface of wood pulp fibers, presumably the primary wall, was not easily soluble even in cuprammonium solution. Also, unlike both the outer layer and inner body of the secondary wall, the primary wall is largely membranous and does not fibrillate, at least on its exterior surface, so that whatever portion of it remains, forms a smooth, protective layer on the outside of the fiber. When the fibers are almost wholly covered with this layer, as is usual in the unbeaten state, adjacent fibers in a wet web of paper are prevented from appreciably adhering together on drying, not only because of the absence of a surface "suspension" on the sheathed part of their exteriors but also because the diameters of the fibers are large compared with the diameter of fibrils subsequently produced by beating. Stiff elements result from large diameters; however, since the surface tension per unit length of element is independent of its diameter, only a relatively small compressive effect on the sheet is noticed with unbeaten stock when the water is removed on drying. To some extent the greater rigidity of the wet fibrous structure also may be the result of the presence of part of the primary wall, and this factor too would prevent the fibers from coming into intimate contact when the sheet is dried.

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[69] L. E. Wise, J. W. Green, and R. C. Rittenhouse, *Tappi*, **32**, 335 (1949).

As beating proceeds, accompanied by the rubbing off of the brittle primary wall and the further wetting and swelling of the fibers, the underlying material becomes more coarsely fibrillated; this not only permits stronger surface tension effects to compact the sheet better, but also results in a greater extent of bonding surface. The rubbing probably also increases the "concentration" of the surface "suspensions," and any cellulosic material that is rubbed off entirely serves as an adhesive filler between the interstices of the larger fibers. Some of the very finest material may possibly also function as a "protective colloid," forming a more stable surface "suspension" by preventing long molecules or fibrils which have been raised from the surface of the fibers from re-embedding themselves.

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[70] O. Maass and W. B. Campbell, *Pulp & Paper Mag. Can.*, **40,** No. 2, 108 (1939).

[71] F. E. Brauns and H. F. Lewis, *Paper Trade J.*, **105,** 35 (Sept. 2, 1937).

When beating exceeds a certain point, a state is reached where the increase in bonding material and facilities for bonding are offset by decreased fiber length and a weakening of the fibers themselves by mashing and reticulation. At this point the pulp reaches the maximum strength.

This composite theory appears to account for all the observed facts known at present about the beating action. The picture includes the following operations to the water-immersed fibers: (1) removing the primary walls, at least in part; (2) loosening underlying elements of the fibers and thus enabling subsequent interlocking of these elements; (3) softening and swelling of the fibers and their fibrils so that they will better fill the space allowed by their neighbors and thus increase the area of contact between them; and (4) creating smaller bodies, either attached to or separated from the fibers, which can nest in the crannies between adjacent elements, thus further increasing contact. The ultimate mechanism of cohesion of the changed structure may be considered a chemical one, if the nature of hydrogen bonding is defined as chemical. Because of the relative spatial positions of the adjoining cellulose chains, presumably the primary hydroxyls play the decisive role in the bonding between them. If the hydroxyls of these chains are hydrated, they do not have much residual attraction for one another. If, however, hydrated chains in close contact with one another lose their water of hydration, they will seek to establish hydrogen bonding with the hydroxyl groups of their immediate neighbors, whether these neighbors belong to the same or to another fiber, thus bonding the fibers and also the fibrous structure together. The great importance of water for this process is evident.

When the bonding is between the more flexible fibrils and smaller elements, the sheet on deformation can adjust itself so that some stress is thereby placed on many bonds before overloading the most stressed. Even if unfibrillated whole fiber surfaces could be made to adhere as strongly to one another, the slightest movement of adjacent fibers after drying would put large strains on the joints because of the rigidity of the thick fibers. In consequence there would be a correspondingly low resistance to a breaking of the structure of a paper which depended for its strength solely on adhesion between surfaces of the fibers rather than also upon interpenetration and cohesion of their smaller and more flexible fibrous elements.

D. RESULTS OF BEATING

The phenomena and changes which take place when pulp is beaten and when beaten pulp is made into paper are many. The more important results of beating can be grouped, for purposes of discusssion, according to the effects on fibers, pulps, and paper. These and some miscellaneous factors will be discussed in the light of what has been said regarding the action of the beater and the foregoing composite theory of beating.

Artificial cellulose fibers do not respond at all to beating because of their solid structure, which cannot fibrillate. Mechanical or groundwood pulp and most "semichemical" pulps (that is, pulps which have been prepared by giving the raw material a mild chemical cook with a resulting yield of over 70%, followed by mechanical reduction to fibrous elements) do not have their structures sufficiently delignified or loosened by the cooking to fibrillate easily. In consequence, these do not respond well to beating; they are merely comminuted. The following discussion applies to naturally occurring cellulose fibers from which the lignin has been substantially removed by one of the conventional pulping processes.

1. Effects of Beating on the Fibers

(1) **Swelling.** An appreciable swelling of the fibers occurs, until the voids and accessible amorphous regions are thoroughly saturated with water. This swelling, of the order of 20 to 30%, does not noticeably increase with beating until the internal fiber structure is loosened, when the fibers may swell rapidly to twice their original diameter.[28]

(2) **Rubbing.** At least a portion of the primary wall, the relatively brittle sheath that surrounds the fiber, is removed.[63] Indeed, usually quite noticeable quantities are removed by the pumping, agitating, and other mechanical actions to which the fibers are subjected after pulping. This exposes an exceedingly fine, almost invisible microscopic fibrillation or fuzz on the underlying secondary wall as shown in Figure 3.

Observations indicate that the primary wall on acid-cooked sulfite pulp is more brittle and comes off more readily than that on alkali-cooked kraft or soda pulps. This may well be a contributing factor in the slower rate of beating which is a characteristic of alkaline pulps in general.

(3) **Cutting.** Wet fibers are not very strong in shear or in tension and may

be cut by the intense pressure developed across clots or fibrages caught by the bars, especially when they are thin or sharp. When the fibers are well rubbed, bruised, and swollen by gentle preliminary beating, they become softened, more slippery, and will stretch more. They do not then cut so easily as do those from a dried pulp that is insufficiently swollen before being subjected to intense bar action.

(4) **Splitting.** The fibrous structure is ultimately unraveled or split, with the formation of fibrils which are visible under relatively low magnification. The manner in which fibers split and fibrillate depends upon their structure. Bast fibers like linen split readily into long, fine fibrils; wood pulps, which have their fibrils lying more or less circumferentially, especially on the outer layer of their secondary wall, tend to produce coarser and shorter fibrils. Many of these break off and, together with the particles from the primary wall and short cells, form a debris which, being mobile, tends to plug the pores in a mass of pulp very effectively when water attempts to flow from or through the mass but to a lesser extent when the mass is vibrated as on a paper machine wire. The newly exposed surfaces immediately adsorb a layer of water.

(5) **Bruising**. Internal splitting (i. e., bruising) results in the penetration of water, which thereupon becomes adsorbed on the newly opened surfaces and keeps them from recrystallizing together again. In consequence, the fibers become more limp and flexible in their wet state. When the fibers are dried, the sorbed water is removed, and most of the split fiber surfaces and some of the previously existing voids or canals may "heal" together again so that the fiber becomes as stiff as or stiffer than before.

(6) **Deformation.** When the consistency of the pulp is high and with equipment that produces a rolling or twisting action, many of the fibers become more or less permanently curled or bent (i. e., deformed) because of their appreciable plasticity when moist.

2. Effects of Beating on the Pulp

(7) **Surface.** According to measurements made by the silvering technique, there is a rapid increase in the specific surface of the pulp, especially during the early stages of beating. This rapid increase appears to be due to the removal of the primary wall; obviously its complete removal would triple the exposed surface. When using the liquid permeability method of measuring the specific surface, Robertson and Mason[72] found that the surface increase is slow at first and rises more and more quickly as

[72] A. A. Robertson and S. G. Mason, *Pulp & Paper Mag. Can.*, **50,** No. 13, 103 (1949).

beating progresses. These findings, based on the Kozeny-Carman[73] equation for flow, seem incompatible with microscopic observation, especially if the silver staining technique or the electron microscope is used, and inconsistent with the corresponding very rapid increase in strength during the early stages of beating.

(8) **Greasiness.** The pulp develops a slimy or greasy feel; it also flows more readily around the tub of an ordinary hollander, and its surface looks smoother. These effects are due to the fibrillation and bruising of the fibers, with the subsequent sorption of water on the freshly made surfaces and crevices of the fibers and their consequent swelling, and also to the reduction of length of the fibers.

(9) **Wetness.** There is an increase in the time taken for water to drain away from a mass of wet pulp placed on a screen and an increased resistance to the passage of further water through the wet mat. The amount of water retained by a given dry weight of pulp under a given pressure has been reported[31] to be greater for beaten than for unbeaten pulp. Several observers,[35,74] however, have found that the quantity of water retained by either pulp under the same pressure is the same, provided that enough time elapses for equilibrium to be reached.

(10) **Flocculation.** When stirred in a dilute suspension of water, well-beaten pulps usually, but not always, disperse more readily than unbeaten pulps; after standing, these pulps do not floc as readily. Fibrillation developed during beating promotes clotting of the fibers in suspension because of the resulting mechanical entanglement upon chance contact. However, this effect is usually more than offset by the concurrent reduction of fiber length during beating which enables the fibers to move and turn in suspension more freely without coming into mutual contact.

(11) **Sorption.** The sorption of most basic dyestuffs, such as methylene blue, in aqueous solution is scarcely affected,[32,40] but with certain direct dyes (such as Purpurin 4B) and also alumina sol and other positive colloids, some increase in sorption does occur, probably, in part at least, because of the increased external surface.

(12) **Equilibrium Moisture.** Beating increases the equilibrium moisture content of the pulp only very slightly.[16,50,75–77] It may be mentioned that most cellulosic materials contain approximately one-eighth additional

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[73] P. C. Carman, *Trans. Inst. Chem. Engrs. (London)*, **15**, 150 (1937).

[74] A. Sedoff, C. V. Holmberg, and E. C. Jahn, *Paper Trade J.*, **109**, 42 (Dec. 28, 1939).

[75] W. B. Campbell and L. M. Pidgeon, *Pulp & Paper Mag. Can.*, **29**, No. 6, 195 (1930).

[76] C. O. Seborg and A. J. Stamm, *Ind. Eng. Chem.*, **23**, 1271 (1931).

[77] J. K. Russell, O. Maass, and W. B. Campbell, *Can. J. Research*, **15B**, 13 (1937).

moisture at a given atmospheric humidity and temperature if approached from a wetter instead of from a drier state. As a rule also, the purer the cellulose is, the less is the moisture content under the same conditions. Some increase in the sorbed moisture would be expected with the greater surface exposed by the splitting of the fibers.

(13) **Copper Number and Viscosity.** The effect of beating on the pulp properties measured by cuprammonium viscosity (degree of polymerization) and copper number (end groups) is open to question. Some observers report that intense beating slightly reduces the viscosity of a solution of the pulp in cuprammonium hydroxide, increasing at the same time the copper number.[78] Negative results have been obtained by other observers. It may be concluded, therefore, that the effect of beating on the chemical characteristics of pulp under normal conditions is not appreciable. However, if the mechanical action is sufficient to disrupt some of the molecules, as happens with dry grinding of pulp, a slight increase in both of the above properties would be expected, as has been found.[58]

(14) **X-ray Pattern.** The x-ray diffraction pattern of the cellulose is unchanged. It has been shown that a very drastic treatment such as mercerization is required to change the pattern,[79] so that beating could hardly be expected to have an effect.

(15) **Concentration of Inert Substances.** The concentration of inert substances, such as sugar, dissolved in water in which the fibers are placed is not appreciably changed by beating.[35] This, incidentally, is not a very sensitive method for the detection of combined water in the presence of adsorbed water. Beating may alter the pH of the suspension appreciably, especially of an alkaline pulp, by squeezing out sorbed chemicals from the interior of the fibers.

(16) **Zeta Potential.** The electrokinetic potential of the pulp is stated to increase.[80] The difficulty of making such measurements with precision has been discussed by Mason.[81] In addition, the exposed surfaces of the fibers increase greatly, and the possible influence of the removal of the surrounding primary wall is uncertain. For these reasons, the reported results would appear to require confirmation.

(17) **Heat of Wetting.** The heat of wetting of dried cellulose when placed in water is not appreciably affected by beating and may be decreased, but crushing cellulose while dry increases the heat of wetting by about 25%.[70]

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[78] C. E. Curran, F. A. Simmonds, and H. M. Chang, *Ind. Eng. Chem.*, **23**, 104 (1931).

[79] C. Trogus, *Verein Zellstoff- Papier-Chemiker u. -Ingenieure, Jahresber.*, **1928**, 140.

[80] K. Kanamaru, *J. Soc. Chem. Ind., Japan*, **34**, Suppl. binding, 39 (1931).

[81] S. G. Mason, *Tappi*, **33**, 413 (1950).

This would indicate that fresh internal surfaces opened up by beating are mostly closed again on drying and that the reformed bonds between adjacent cellulose micelles are not capable of being opened again by wetting. In consequence, if pulp is beaten before drying, it is considerably less reactive.

3. Effects of Beating on the Paper

(18) **Density.** The fibrous structure of paper made from beaten stock will shrink more on drying and give a harder, more dense, and less permeable sheet. This phenomenon, which increases in proportion to the logarithm of the length of the beating time,[8,29] is due to the production of the finer fibrils, the softening of all the elements, and the drawing together of these elements during drying by surface tension. Whether the sheet is permitted to shrink freely or is dried under tension does not appear[82] to influence the apparent density of the structure if the thickness of the sheet is measured with a micrometer having a ballpoint pressure foot.

(19) **Opacity.** The opacity of the paper decreases. Very well beaten pulp forms a paper quite translucent and, incidentally, one less pervious to oil (e. g., greaseproof paper or imitation parchment). Additional beating and heavy calendering form a transparent paper (e.g., glassine). The opacity of a paper is dependent, among other things, on the extent of the solid–air interfaces present in its structure. These in turn depend on the total specific area of its components less the area in solid contact. With beating, the latter increases more rapidly than does the former.

(20) **Color.** A given quantity of dyestuff will give an appreciably greater intensity of color to finished paper made from beaten stock, and a white sheet will appear to be darker than one from the same stock lightly beaten. This follows from the changes noted in the preceding paragraph.

(21) **Sizing.** The degree of sizing of paper (i. e., resistance to aqueous fluids) with a given quantity of sizing materials, such as rosin size and papermaker's alum, improves markedly to begin with because of the greater compactness of the wet structure. However, a very well-beaten stock, such as that prepared for glassine, becomes difficult to size, probably because of the very low retention of any added materials other than sugars or polysaccharides, especially if the added materials like sizing agents are hydrophobic. Even starch is then poorly retained.

(22) **Strength.** Paper made from beaten pulp will have a higher tensile and bursting strength and will stretch more before rupture, for reasons dis-

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[82] G. F. Glover, P. F. Ray, and E. J. Pritchard, *World's Paper Trade Rev.*, **135**, 51 (1951).

cussed earlier in this chapter. Excessive beating under certain conditions will reduce the bursting strength from its maximum value but seldom the tensile strength. Except for a rise in the resistance of the paper to tear, as is frequently observed during the early stages of beating in practice, the tearing strength progressively diminishes, mainly because of shortened fibers and increased sheet density. As beating increases, the ability of the paper to withstand repeated folding rapidly rises to a maximum, then usually diminishes after the paper becomes brittle.

4. Factors Affecting the Rate of Beating

(23) **Chemical Composition.** Fibers that contain considerable quantities of hemicelluloses beat more rapidly than purified fibers. Pulp hydrolyzed with acids also beats faster. These and other chemical matters are discussed later in this section.

(24) **Temperature.** An increase in the temperature of the pulp decreases the rate of beating; conversely, low temperatures promote more rapid beating.[83,84] Also, when beaten stock is heated especially to a high temperature, its wetness is considerably reduced.[85] These effects which have been well known in practical papermaking for a long time, are both probably concerned with the fact that, as with most other adsorption phenomena, a decrease in temperature enhances the adsorption of water on exposed cellulose surfaces and thus promotes greater swelling and fibrillation, especially microfibrillation.

(25) **Effect of Predrying.** Pulp that has been dried is much more difficult to beat and, with treatment identical to an undried pulp, results in a weaker, softer, bulkier, and more opaque sheet. When pulp is derived from paper or "broke" by repulping, these effects are accentuated. It seems likely that when cohered dried fibers are forcibly parted, especially if well beaten and if not well soaked in water, the most efficient fibrils and microfibrils (that is, the ones that took part in the previous bonding) are stripped off their surfaces.[63] Furthermore, the drying of beaten fibers also causes their internal splits and voids to recrystallize or heal, giving a more compact and stiffer structure. Considerable mechanical treatment is required to break a substantial number of these internal bonds, to permit the penetration of water again, and to refibrillate the surfaces. During the course of this

[83] A. Noll, *Papier-Fabr.*, **35**, Tech.-wiss. Tl., 393, 401 (1937).

[84] O. K. Ronney and C. E. Libby, *Tappi*, **34**, 223 (1951).

[85] T. R. Le Compte, *Paper Trade J.*, **93**, 42 (Oct. 1, 1931).

treatment, the fibers are further cut and shortened so that the drying of moist pulp constitutes practically an irreversible process.

(26) **Beating in Other Liquids.** The progressive decrease in the strength of the resulting paper when pulp is beaten in liquids progressively less polar than water, described by Strachan,[86] Kress and Bialkowsky,[40] and Edge,[65] has already been mentioned. The beneficial effect of formamide on beating has been confirmed by Musser and Engel.[87] During beating, the degree of "peptization" or dispersion of the elements on the surfaces of the cellulose will depend on, among other things, the attraction of the liquid to the surfaces of the hydrophilic cellulose. Oils and benzene are attracted not at all, whereas formamide is even more strongly attracted than water.

5. Phenomena Relating to Beaten Pulp

(27) **Effect of Temperature.** Clark[46] has found, contrary to the findings of Nakano as discussed by Le Compte,[85] that the strength and other qualities of the resulting paper may not be impaired by heating a beaten stock. Also, the wetness of the stock is not recovered by later soaking it for several days, but it may be recovered, at least in part, by vigorous stirring of the stock at normal temperatures.

Jayme[41] found that the degree of swelling of pulp was decreased by boiling for an hour and that the strength of the sheets was somewhat diminished. The wetness of the pulp was not greatly improved by soaking the boiled pulp in cold water for a day. Lyne and Gallay[88] also found that heating a beaten pulp as a suspension and again also heating the test sheets after forming and especially after pressing them, resulted in a decrease in tensile strength and an increase in the bulk and the tear. It is evident that wetness of pulp will be decreased by boiling, because the surface "suspension" would be dehydrated and collapse and, if it is conceded that the surface tension effect of the water as it is removed from between the fibers on drying is sufficient to raise most of the fibrils and smaller components of the "suspension," this may be the reason why boiling does not appreciably affect the strength of the resulting paper in some instances. If the fibers in a moist sheet are heated and are left with insufficient water between some elements to re-form the suspension, and are then dried, it is clear that the density of the paper will be less, and consequently the tensile strength will be decreased and the tear increased.

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[86] J. Strachan, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **6**, 181 (1925).

[87] D. M. Musser and H. C. Engel, *Paper Trade J.*, **115**, 33 (Aug. 20, 1942).

[88] L. M. Lyne and W. Gallay, *Tappi*, **33**, 429 (1950).

(28) **Addition of Inert Materials.** The incorporation in pulp of any filler, such as china clay, calcium sulfate, or chalk, reduces the strength of paper made from it. The addition of oils or waxes has the same effect, but to a greater degree. Resin size weakens the sheet except sometimes with an unusually weak, lightly beaten pulp when the adhesion provided by the resin exceeds the natural cohesion of the fibers. Sizes made from bituminous emulsions have a similar weakening effect on strong, well-beaten pulp but similarly may improve the strength of weak pulps such as from old paper often used for making some kinds of boxboards, after scarcely any beating. On the other hand, the addition of certain hydrophilic materials, such as locust bean and guar gums,[89] methyl[90] and carboxymethyl[91] celluloses, soluble resins,[92] hemicelluloses,[93] and cooked starches,[94] improves the strength of the resulting sheet unless the pulp is very highly beaten.

These effects follow because the natural bonding of well-beaten fibers by fibrillar entanglement and recrystallization is a very efficient process. The addition of suitable adhesive material will supplement the natural bonding if the pulp is not well prepared, but otherwise it will be a hindrance to the natural bonding.

(29) **Addition of Electrolytes.** Cohen,[95] in a recent careful study, found that monovalent cations added to the pulp cause a slight increase in the strength of the sheet, divalent cations have little effect, and tri- and tetravalent cations cause a substantial reduction in strength. Water flows through pulp more readily in the presence of electrolytes, the effect increasing with valency of the cation. The adverse effect of papermaker's alum on sheet strength and on wetness has been known for a long time. Also, it may be observed that when alum is added to the tub of a beater, the level of the stock in front of the roll is lowered appreciably because the mass becomes less fluid.

These results could be expected from a knowledge of the flocculating effects of polyvalent cations on hydrophilic colloid suspensions, if the same principles are applied to the two-dimensional "suspension" on the surfaces of the fibers. The weakening effect of the trivalent cations is probably due to their causing a precollapse (analogous to precipitation) of the microfibrils on the fibers. Thus, when the microfibrils are collapsed and the fibers are placed and dried together, even the surface tension effect of the departing water cannot re-elevate the normal quota of microfibrils to form the "suspension" to bond with that on neighboring surfaces. The slight strengthening effect observed with monovalent cations may be due to their displacing the divalent cations (calcium) normally present, and thus facilitating the "suspension" of the microfibrils.

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[89] B. W. Rowland, *Paper Ind. and Paper World*, **27**, 1398 (1945).

[90] D. M. Musser and H. C. Engel, *Paper Trade J.*, **115**, 85 (Aug. 20, 1942).

[91] S. R. H. Edge, *Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. & Ireland*, **27**, 189 (1946).

[92] C. G. Weber, M. B. Shaw, M. J. O'Leary, and J. K. Missimer, *Paper Ind. and Paper World*, **30**, 83 (1948).

[93] L. E. Wise, *Paper Ind. and Paper World*, **29**, 825 (1947).

[94] J. P. Casey, *Paper Ind. and Paper World*, **26**, 1277 (1945).

[95] W. E. Cohen, *Paper Trade J.*, **132**, 19 (June 22, 1951).

For the same reasons, materials which have strong flocculating and dispersion actions on hydrophilic colloids also profoundly affect the strength of paper. It is known that the addition of tannin[96] has a marked depressant effect on the strength of paper and on wetness of the pulp. On the other hand, Cohen and others in his laboratory [97] found that sodium hexametaphosphate in concentrations of about 0.0015 N improved the strength of several pulps in the order of 15% and the air imperviousness of resulting paper as much as 70%.

(30) **Bacterial Action.** Keeping moist beaten stock sterile and wet for months at normal temperatures does not appear to alter its character.[98] However, keeping beaten pulp for a day or two in a stock chest (i. e., a large vat), where it is subject to bacterial action, usually reduces its wetness and makes it drain faster on the paper machine; keeping unbeaten stock in a chest under the same conditions usually increases the ease with which it can be beaten.

It appears that when cellulose-consuming bacteria are present, they would first consume the microfibrils from the surfaces of the beaten pulp and so reduce its wetness and the strength of the paper. In the case of an unbeaten stock, it is conceivable that under certain conditions the bacteria would weaken or even cleave the internal structure of the fibers and permit easier separation of its components and consequently faster beating.

E. PULP CHEMISTRY AND PAPERMAKING PROPERTIES

In the cooking and bleaching of pulps and in certain chemical tests where complete solution is not attained, the chemical operations are progressive in depth (topochemical), and the results depend to a degree on the chemical and physical nature of the successive layers accessible to the chemical reagents. Other important factors are the heterogeneity of the chemical constituents of most pulps, varying from highly active to inert, and the disproportionate ease with which the amorphous zones are chemically attacked or dissolved as compared with the crystalline zones. Another complication is the empirical nature of the tests themselves, the results of which are appreciably altered by differences in the chosen times and temperatures of reaction and the concentrations of the reactants. Papermaking properties of individual pulps reside mainly in the exposed surfaces of the fibers. This is especially so under modern conditions where most of the exterior of the fibers are not extensively split open, so that it is difficult to deduce papermaking properties from the chemistry of the entire fibrous bodies which, on the contrary, derives mainly from the interior components. Moreover, because of the nature of the paper structure, a number, perhaps not less than five, of distinctly different properties of a pulp (described earlier in this chapter under "Pulp Testing") must be determined and considered together before an unknown sample can be characterized for its papermaking qualities with any degree of certainty. Accordingly, it would seem reasonable to suggest that mere chance plays quite an important role in many and varied correlations which have been found to exist between one or two individual chemical tests and the papermaking properties of the pulps, especially since exceptions are so frequently found.

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[96] H. P. Dixon, Jr., *Paper Trade J.*, **111,** 29 (July 18, 1940).

[97] W. E. Cohen, Gwenneth Farrant, and A. J. Watson, *Paper Trade J.*, **133,** 16 (July 27, 1951).

[98] *Second Report of Pulp Evaluation Committee to the Technical Section*, Paper Makers' Assoc. Gt. Brit. & Ireland, London, 1936, especially p. 85.

As far as papermaking is concerned, the main function of applying chemistry to pulps is to provide an understanding of the reasons underlying differences in their physical properties or to furnish a basis for process control rather than to provide for an actual evaluation of the pulps. This limitation should be kept in mind during the following discussion of the three main groups of chemical tests which have proved the most interesting.

1. Degree of Polymerization

The tests related to degree of polymerization (D.P.) include viscosity, chain-length distribution, alpha-cellulose content, and copper number.

It may be said that, in general and in accordance with Schur and Lewis,[99] sulfite pulps with a high D.P., that is, around 1500 (which corresponds to a TAPPI viscosity of a 1% solution in cuprammonium of about 70 centipoises), resist cutting during beating and can be well fibrillated before becoming too short. The pulp probably would be especially suitable for currency and high-class papers such as for records of deeds where permanency of the paper is also an important factor. Pulp with a low D.P., say 600 (10 centipoises, TAPPI) or below, will not be resistant to cutting and will beat much faster. The resulting paper will be relatively soft, bulky, weak, absorbent, and opaque and suitable for featherweight papers often used for novels. This is so to some extent even if the low viscosity is achieved by degrading the pulp with a mineral acid,[100] but it should be emphasized that if the D.P. of a pulp has been reduced by a greater degree of cooking and in another case "artificially" reduced by acid hydrolysis, their characters will differ considerably. The entire cellulose structure, including existing or potential fibrils, will be weakened uniformly throughout by treatment with the acid. A pulp with an intermediate D.P. is desirable for papers having a balance of properties, good strength, and good formation (which in practice requires that the pulp be shortened somewhat during beating), for example, fine writing papers.

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[99] M. O. Schur and H. F. Lewis, *Tappi*, **33**, 392 (1950).

Corresponding figures for the D.P. of sulfate pulps, or of alkaline-prepared pulps having similar characteristics as far as beating and strength are concerned, are much lower, perhaps only half as much.[101] Jayme[41] holds the view that the surfaces with the highest D.P. form the strongest bonds, and that well-beaten sulfate pulp is much stronger than well-beaten sulfite pulp of the same D.P. because the D.P. of surface material on the sulfite is much lower. However, this view does not appear to account for the fact that if the two pulps were given only a small degree of beating, under ordinary circumstances paper made from the sulfite pulp would be much the stronger, as would be expected from the composite theory of beating previously discussed, since the sulfite pulp, having the lower D.P., would accordingly provide surfaces with greater cohesiveness.

A highly purified wood pulp, that is, one high in alpha-cellulose content, is exceedingly difficult to beat.[102] This too would be expected from the composite theory because of the relative difficulty of forming a substantial surface suspension with only long-chain molecules, the short ones having been removed by the purification process. On the other hand, rag pulps which have the same or a higher alpha-cellulose content, especially if from well-worn materials, are not so difficult to beat. This is due to the different manner in which the various fibers disintegrate under the action of the beater. Cotton and especially bast fibers, such as linen, are frayed out and unraveled into a mass of very fine, long fibrils by beating, whereas wood breaks up into relatively coarse, short particles or, at best, into coarse fibrils.

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[100] D. M. Musser and H. C. Engel, *Paper Trade J.*, **113**, 31 (July 10, 1941); **114**, 29 (Apr. 9, 1942).

[101] If chips from the same wood are pulped to the same degree of lignin removal, despite the fact that the viscosity of the sulfate pulp will be substantially less than that of the sulfite pulp, the zero-span tensile strength of the former will be significantly higher. This evidence suggests that the factor used for converting the viscosity of differently prepared pulps to D.P.'s may not be independent of their preparation as is generally assumed.

[102] G. A. Richter, *Ind. Eng. Chem.*, **23**, 131, 266 (1931).

Degraded cotton rags, a bleached coniferous sulfite, or a hardwood kraft may each have the same measured viscosity and yet have widely different beating qualities and yield quite different papers. Thus, except possibly as a control test applied to pulps from the same source and prepared under the same conditions, the viscosity test is of little or no value by itself in predicting their papermaking qualities. However, it can be stated that a pulp with both a high D.P. and a high hemicellulose content can usually be made to yield strong papers.

The distribution pattern of the molecular chain lengths in cellulose has also failed to show promise for evaluating papermaking qualities. This is not surprising because, by analogy, Clark,[11] as already mentioned, has shown that paper made from a mixture of long and short fibers had very similar properties in all respects to paper made from fibers of uniform length equal to the weight-average fiber length of the mixture.

2. Hemicellulose Content

Tests related to hemicellulose content include beta- and gamma-cellulose contents as determined by the Cross and Bevan procedure (see Chapter XII), solubility of the pulp in alkalies of various strengths, and pentosan and polyuronide contents.

It is well known that impure fibers, for example, unbleached pulps and especially ordinary straw pulps with their high hemicellulose content, beat more rapidly than purer fibers. The pentosan content of the pulps appears to have a marked influence on beating,[103] but Klingstedt[104] and March[105] point out that the factor is the proportion of alkali-soluble material in the pulp rather than the pentosan content. Bleaching removes some of the hemicellulosic materials, especially if the pulps have been subjected to a caustic extraction during the bleaching process. This usually results in slower beating of the pulp. However, if the original pulp was somewhat raw to begin with, then removal of lignin by bleaching may increase the rate of beating. Alkali-cooked pulps from coniferous woods have more hemicellulose removed than sulfite pulps, and accordingly they beat more slowly. On the other hand, if hardwood pulp is prepared by the sulfite process (which is seldom) the resulting pulp is both weak and difficult to beat. With deciduous woods, it may be that the material is so degraded by the acid cooking liquor that it becomes soluble, and therefore nearly all the hemicellulose on the surfaces is removed.

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[103] G. H. Young and B. W. Rowland, *Paper Trade J.*, **97**, 44 (Oct. 12, 1933).

[104] F. W. Klingstedt, *Svensk Papperstidn.*, **40**, 412 (1937).

[105] R. E. March, *Paper Trade J.*, **127**, 51 (Oct. 21, 1948).

Cottrall[38] has recently presented a comprehensive review of the effect of hemicelluloses on the papermaking qualities of wood pulp, and additional data showing that pulp becomes less responsive to beating and yields a weaker sheet as hemicellulose is removed. He also shows that the gamma-cellulose content of a number of different kinds of wood pulp correlates quite well with the resulting papers. He agrees with Jayme and Lochmüller-Kerler[106] that there is an optimum hemicellulose content for pulps above and below which the strength of the resulting sheets is less. March[105] also found this to be the case. Cottrall refers to the linear relationship between the pentosan content of softwoods and their swelling capacity found by Young and Rowland[103] and subscribes to an opinion that the main role of hemicellulose is its action as a plasticizing agent for the fibers. This view is in accord with the findings[107] that the addition of hemicelluloses to pulps deficient only in this respect has a relatively small, but nevertheless significant, beneficial effect on the rate of beating and the resulting strength of the sheet.

With respect to the three Cross and Bevan celluloses, Giertz[108] has presented evidence to show that the alpha-cellulose content of wood pulp produced by a wide range of cooking conditions is remarkably constant—at 43% for spruce. It would appear to represent the highly crystalline and resistant cellulose composing the "strings" or micelles in the secondary wall of a fiber, which may be seen in an electron microscope after disrupting the fiber by ultrasonic treatment, as uniform bodies about 75 A. thick.[109] In the fiber they lie together as bundles, and between these crystalline elements are amorphous regions containing the hemicellulose or the gamma fraction, which Giertz showed corresponds closely with the quantity of easily hydrolyzable material in a number of pulps, as determined by Nickerson's method. The beta-cellulose fraction becomes appreciable only after the pulp has been subjected to degradation as with acids or prolonged cooking. Consequently, this fraction would appear to represent any short-chained fragments derived from the crystalline cellulose by cleavage. Rånby[110] has confirmed this with further electron microscope and x-ray studies of the various fractions.

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[106] G. Jayme and E. Lochmüller-Kerler, *Papierfabr. Wochbl. Papierfabr.*, **1944**, 223.

[107] H. E. Obermans, *Paper Trade J.*, **103**, 83 (Aug. 13, 1936).

[108] H. W. Giertz, *Proc. Tech. Sect., British Paper & Board Maker's Assoc.*, **33**, 487 (1952) Part 3; *World's Paper Trade Rev.*, **136**, 1451 (1951).

[109] B. G. Rånby, *Tappi*, **35**, 53 (1952).

Giertz[111] has also pointed out that since the pentosan and noncellulosic material is contained mainly in the noncrystalline parts of the fibers, it may not itself influence beating but rather be a proportionate indication of the presence of amorphous cellulose which can swell and be beaten much faster than the crystalline portions. He questions Wurz's conclusion[51] that the presence of pectins and polyuronides is of primary importance in a pulp suitable for making a good greaseproof paper (a hard transparent sheet) because of the almost insignificant percentage—about 2%—required. Giertz suggests that because these constituents are so easily hydrolyzed by adverse cooking conditions, their presence is merely a sign that the sulfite cooking condition was mild enough that a large proportion of hemicellulose, and thus the original amorphous cellulose, is left in the fibers. The greater amorphous cellulose content will permit the pulp to swell and be beaten more easily, and thus, when the sheet is dried, the fibers will collapse to give both the fibers and the sheet a dense, translucent structure. This view appears to be in good accord with observed phenomena and may explain anomalies in the relation between the chemical analysis of many pulps and the strength of the resulting papers.

3. Lignin Content

The usual tests for lignin content comprise the chlorine demand of the pulp, its bleachability, and its permanganate number.

For a long time it was thought that the presence of lignin in "strong," i.e., relatively undercooked, pulps was responsible for their generally higher strength, and it was common to grade pulps on that basis. However, it has become clear that if the lignin was progressively removed with chemicals like chlorine dioxide[112] and sodium chlorite[113] that did not appreciably impair the cellulose and hemicellulose content, the strength of the pulps was in fact improved.

Raw pulps, such as are prepared by "semichemical" processes and which ontain a large proportion of their original lignin content, do not beat quickly nd do not yield very strong papers. It would appear that if present in uantity, for example in a wood pulp having a yield of upwards of 70% of he original wood substance, the lignin continues to bind the structure of he individual fibers together so tightly that they cannot be fibrillated asily. Thus, as with artificial cellulose fibers, attempts to beat them merely ause a reduction in their size. In either case, even with the addition of mucilage or other binding agent, with the complete absence of fibrillation on viscose or only the sparse fibrillation developed on highly lignified pulp fibers, no tough cementing action between the fibers can be achieved.

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[110] B. G. Rånby, *Svensk Papperstidn.*, **55**, 115 (1952) (in English).

[111] H. W. Giertz, *Cellulosa och Papper SPCI 40th Anniversary No.* **1908–1948**, **417** (1948).

[112] E. C. Jahn and C. V. Holmberg, *Paper Trade J.*, **114**, 203 (Apr. 23, 1942).

[113] G. Jayme, *Papier-Fabr.*, **40**, 137, 145 (1942).

4. Cooking Reactions

When cellulose-containing material is cooked to make pulp, the components of the fibers and of the encrusting material are attacked at different rates. The proportionate rate of attack on different components of the fibers also depends on the nature of the cooking liquor and on the time and temperature schedule employed. It should be pointed out that although the alkaline processes avoid degradation by acids, degradation due to heat is greater because of the higher cooking temperatures used.

Varying the acid concentration and calcium content in a sulfite cook or the alkali concentration and degree of sulfidity (which has a protective influence on the fibers) in a sulfate cook yields pulps of various compositions as well as kinds. The attack is mainly on the amorphous or less crystalline parts of the fibers so that, as Giertz points out, the quantity of amorphous cellulose remaining is an important determining factor in the papermaking quality of the pulp.

The removal of lignin from the fibers by the cooking liquor parallels, to some extent, the attack on the different cellulose components. In consequence, by varying the cooking conditions, pulps can be produced having the same chlorine demand or lignin content and perhaps the same hemicellulose content, but having quite different papermaking characteristics.

A coniferous pulp prepared by the sulfite process (acid) with a moderate degree of cooking, as determined by its lignin content, beats more rapidly than a pulp prepared by an alkaline cook (e.g., soda or sulfate process) and having the same lignin content. Mitscherlich pulp (pulp prepared by a relatively mild slow sulfite cook) cooked to the same degree beats still more rapidly.

In accordance with the composite theory of beating, when pulp is produced by any mild process giving a high yield, or by an acid process which tends to hydrolyze the material, there is more short-chain material exposed or created on the outer surfaces. This will form a more "concentrated" and, hence, a more cohesive surface "suspension"; conversely, a caustic treatment, which normally removes the short-chain material and which, unlike an acid, does not effect hydrolysis of the high D.P. material, gives pulp with much less cohesiveness because of the longer chain lengths and thus a lower "concentration" on the exposed surfaces. (In the case of the seldom-made hardwood sulfite pulps, as already mentioned, the short-chain material may be so hydrolyzed that it is dissolved away.) At the same time, consideration must also be given to the effect of the pulping process on the intrinsic strength of the fibers and fibrils. It follows, therefore, that pulp prepared from hardwoods or softwoods by the mild neutral sodium sulfite process which gives a relatively high yield, is exceptionally strong as regards fiber structure and its possession of considerable short-chain adhesive material and amorphous cellulose. Pulp made with the normal (acid) sulfite process is weakened in fiber structure, but, if a softwood, it too beats rapidly, presumably because of hydrolysis or shortening of the material remaining on the surface of the fibers. Soda and especially sulfate pulp retain their fibrous structural strength to a great extent, but, because of the dearth of short-chain material and amorphous cellulose on the outer surfaces of the fibers, beat relatively slowly. If both the sulfite and the sulfate processes are applied to the same softwood chips, then a carefully produced sulfate pulp, because of its greater D.P. and thus greater intrinsic strength, after extended beating to develop fibrillation and cohesion, can be made ultimately into a considerably stronger paper.

Chapter IX

DERIVATIVES OF CELLULOSE

A. REACTIVITY AND REACTIONS OF CELLULOSE

Harold M. Spurlin

The usefulness of cellulose depends not only on the excellent physical properties of cellulose itself, but also on its ready transformation into derivatives. These derivatives are useful because of their solubility characteristics not possessed by cellulose itself, their ease of forming at high temperature, or their greater softness and flexibility.

Many different features of cellulose behavior need to be considered if cellulose reactions are to be understood. The chemical nature of cellulose (Chapter III) and the structure of cellulose fibers (Chapter IV) are obviously important. Many peculiarities associated with individual reaction conditions will be treated at length in later Sections of this Chapter IX. Some ideas about the nature of forces holding the fiber structure together can even be gathered from the nature of fiber–fiber interactions in paper (Chapter VIII). In spite of the fact that some repetition is involved, it appears wise to devote this Section A to a unified treatment in an effort to reconcile the many apparently inconsistent experiments and interpretations thereof to be found in the literature. The viewpoint adopted here owes much to the influence of Staudinger. However, it is believed that a more realistic attitude is expressed, especially in questions that deal with the uniformity of reaction of fibrous cellulose.

The topics considered are: (1) uniformity of reaction, with special emphasis on the nature of derivatives prepared in homogeneous solution; (2) the influence of fiber structure on uniformity; and (3) chemical factors which limit the attainment of uniform products.

Almost all of the commercially important cellulose derivatives are either esters or ethers, prepared by reactions typical of compounds containing hydroxyl groups. Even with those derivatives that are not esters or ethers, such as N_2O_4-oxidized cellulose or derivatives in which the hydroxyl group has been replaced by halogen, amino, or other groups, the methods of preparation are exactly analogous to those of similar compounds of low molecular weight. The peculiarities of cellulose reactions are thus not due to any characteristic difference between the innate reactivities of the hydroxyl groups of cellulose and the hydroxyl groups of other types of compounds. Rather, the problems encountered are due to two main factors: (1) The cellulose hydroxyls may not be available for reaction because the crystallinity or insolubility of the cellulose hinders access of the reagent to the hydroxyl groups; (2) excessive amounts of degradative side reactions must be avoided because cleavage of the cellulose chain would result, giving products with unsatisfactory properties. Fortunately, the degradation reactions may be held within acceptable bounds in the important cases. Most of the technical problems of cellulose reactions thus center about the question of availability of the hydroxyl groups for reaction. Sometimes, as in the case of direct esterification with acetic acid, the lack of availability simply prevents the reaction from going in a satisfactory manner. More often, difficulty arises because the differences in accessibility of different portions of the sample result in very nonuniform products. Much of the science of cellulose derivatives is concerned with methods designed to hold this nonuniformity within acceptable bounds.

1. Uniformity of Substitution

Care is necessary in defining the uniformity of a cellulose reaction. The technologist usually has a clear idea of what is meant by a uniform product. It will be completely soluble in a variety of solvents. Solutions, films, or molded articles will be clear and sparkling, which means that they will be free of suspended matter and will have little tendency to separate into two phases. A more exact consideration will soon demonstrate that even though the above conditions are fulfilled, no cellulose derivative can be really uniform. In fact, statistical considerations show that in no sample of a partially substituted cellulose derivative will there be two identical molecules of long chain length.[1] This variation in arrangement of substituents will be superimposed on a distribution of chain lengths and on differences in degree of substitution (D.S.) between different cellulose chains.[2]

The important question of evaluation of uniformity will depend on a definition of a "perfectly" uniform material and then on some criteria for the degree of deviation from this norm. Uniformity of chain length will be treated in Chapter X-D. The discussion of uniformity of substitution in this Section A of Chapter IX will be based on the following definition of uniformity of a cellulose derivative: The highest possible degree of uniformity is that resulting when every anhydroglucose unit has had an equal amount of exposure to the reagents involved. According to this definition, products of the same degree of substitution and the same molecular weight might be different in properties because of a difference in the manner of arrangement of substituents along the cellulose chain, and yet each product would be considered uniform. This state of affairs is quite possible; uniform cellulose acetates of the same degree of substitution but prepared in different manners actually differ appreciably in properties.[3] This difference is due to varying extents of reaction of the primary and the secondary hydroxyls. (See also Section C of this Chapter IX.)

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[1] H. M. Spurlin, *Trans. Electrochem. Soc.*, **73**, 95 (1938).

[2] A. J. Rosenthal and B. B. White, *Ind. Eng. Chem.*, **44**, 2693 (1952).

The definition of uniformity of reaction adopted here, namely, equality of ease of access of the reagents to the individual anhydroglucose units, naturally brings up the question of whether this equality is attainable. The answer appears to be definitely yes. Modern polymer research is entirely in harmony with the concept that individual segments of a dissolved polymer chain will have the same reactivity as a molecule of low molecular weight and similar structure. Furthermore, the influence of other portions of the molecule on the reactivity of a given group will decline very rapidly with increasing distance from that group. An example may be taken from the field of polymerization: The rate of interaction of monomer with the end of a growing polymer chain during copolymerization depends almost entirely on the nature of the terminal monomer group, and not on the rest of the chain.[4] The hypothesis that the individual anhydroglucose units of cellulose or one of its derivatives in solution are equally available for reaction may therefore be accepted with confidence.

It is equally certain that this uniformity of access will not be possible if fibrous or crystalline cellulose reacts in a heterogeneous manner. Even in this case a product meeting the above definition of uniformity is possible in the case of an equilibrium reaction or in the case of complete reaction. If the reaction equilibrium is at some point short of complete substitution, ease of access may not have been equal at the beginning; however, if sufficient time is allowed, complete access to all hydroxyls may be obtained.

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[3] C. J. Malm, L. J. Tanghe, B. C. Laird, and G. D. Smith, *J. Am. Chem. Soc.*, **75**, 80 (1953).

[4] T. Alfrey, Jr., J. J. Bohrer, and H. Mark, *Copolymerization* (High Polymers, Vol. VIII), Interscience, New York-London, 1952.

The quantitative evaluation of degree of uniformity of a product depends on the development of suitable experimental methods and on correct mathematical interpretation of the results. Since many misleading statements in the literature are based on the wrong mathematics, it is desirable to discuss in detail the nature of the distributions of substituents that can be expected.

(a) CALCULATION OF THEORETICAL ARRANGEMENT OF SUBSTITUENTS

If the principle of equal availability of all anhydroglucose units is accepted, some important conclusions can be reached about the arrangement of substituents along the chain. The nature of the substitution on an anhydroglucose unit will be governed by probability considerations. The commercially important partially substituted derivatives will be expected to have higher local concentrations of hydroxyl groups along some portions of the chains than along others even if they are uniform in the sense used here. These fluctuations of composition undoubtedly have much influence on the properties of the products. For instance, the possibility of microbial attack appears to be associated with the presence of unsubstituted anhydroglucose units along the chain (see Chapter III-C-5). Also, the outstanding physical properties of cellulosic plastics are possibly due to these local high concentrations of hydroxyl groups. There has therefore been a great amount of effort expended on the study of the distribution of substituents along the cellulose chain.

The nature of this distribution is easily calculated on the basis of the assumptions that (1) availability of all anhydroglucose units is equal, (2) the influence of the state of reaction of one hydroxyl on the reactivity of another declines very rapidly with increasing distance between the two, (3) the ratios of the reaction rate constants to one another remain constant throughout the reaction, and (4) end-group effects are negligible. If assumption (3) is fulfilled and the back reaction is negligible, the distribution of substituents at a given degree of substitution will be the same as that obtained in first-order reactions of the hydroxyl groups with nonvarying reaction constants.

All of the available data on distributions controlled by the rates of reaction of the three sorts of hydroxyls may be correlated if assumption (2) is modified to read: The only interference between hydroxyls occurs between positions 2 and 3 of the same anhydroglucose unit. With this proviso, the distribution in the case when only one type of substituent is involved may be described by five reaction rate constants: k_2, k_3, and k_6 for nitial reaction at positions 2, 3, and 6 of the anhydroglucose ring; k_a for reaction at position 3 if position 2 is substituted; and k_b for reaction at position 2 if position 3 is substituted. The total substitution, in substituents per anhydroglucose unit, will be called S. The fraction of unsubstituted anhydroglucose units will be designated s_0; the fraction monosubstituted at position 2, 3, or 6 will be designated s_2, s_3, or s_6; the fraction disubstituted at positions 2 and 3, 2 and 6, or 3 and 6 will be designated $s_{2,3}$, $s_{2,6}$, or $s_{3,6}$; and the fraction trisubstituted will be designated $s_{2,3,6}$. The following symbols are also useful in simplifying the writing of equations:

$$M = \frac{k_2}{k_2 + k_3 - k_a} \tag{1}$$

$$N = \frac{k_3}{k_2 + k_3 - k_b} \tag{2}$$

The equations for the fractions of anhydroglucose units that are substituted in various manners are:

$$s_0 = e^{-(k_2 + k_3 + k_6)t} \tag{3}$$

$$s_2 = Me^{-(k_a + k_6)t} - Me^{-(k_2 + k_3 + k_6)t} \tag{4}$$

$$s_3 = Ne^{-(k_b + k_6)t} - Ne^{-(k_2 + k_3 + k_6)t} \tag{5}$$

$$s_6 = e^{-(k_2 + k_3)t} - e^{-(k_2 + k_3 + k_6)t} \tag{6}$$

$$s_{2,3} = e^{-k_6t} - Me^{(k_a + k_6)t} - Ne^{-(k_b + k_6)t} + (M + N - 1)e^{-(k_2 + k_3 + k_6)t} \tag{7}$$

$$s_{2,6} = Me^{-k_at} - Me^{-(k_a + k_6)t} - Me^{-(k_2 + k_3)t} + Me^{-(k_2 + k_3 + k_6)t} \tag{8}$$

$$s_{3,6} = Ne^{-k_bt} - Ne^{-(k_b + k_6)t} - Ne^{-(k_2 + k_3)t} + Ne^{-(k_2 + k_3 + k_6)t} \tag{9}$$

$$s_{2,3,6} = [1 - e^{-k_6t}]\,[1 - Me^{-k_at} - Ne^{-k_bt} + (M + N - 1)e^{-(k_2 + k_3)t}] \tag{10}$$

$$S = 3 - Me^{-k_at} - Ne^{-k_bt} - e^{-k_6t} + (M + N - 2)e^{-(k_2 + k_3)t} \tag{11}$$

It is frequently convenient to consider the case where all reactivity constants are equal. In this case, a notable simplification of the equations results, and they may be solved in terms of S.[5] These simplified equations follow:

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[5] T. E. Timell, *Studies on Cellulose Reactions*, Esselte A/B, Stockholm, 1950; also, *Ing. Vetenskaps Akad., Handl.*, No. 205, Stockholm, 1950.

If $k_2 = k_3 = k_6 = k_a = k_b$

$$s_0 = \left(1 - \frac{S}{3}\right)^3 \tag{12}$$

$$s_2 = s_3 = s_6 = \frac{S}{3}\left(1 - \frac{S}{3}\right)^2 \tag{13}$$

$$s_{2,3} = s_{2,6} = s_{3,6} = \left(\frac{S}{3}\right)^2\left(1 - \frac{S}{3}\right) \tag{14}$$

$$s_{2,3,6} = \left(\frac{S}{3}\right)^3 \tag{15}$$

If no mutual interference with reactivity at positions 2 and 3 is encountered, $k_2 = k_b$, $k_3 = k_a$, and $M = N = 1$. If the interference between reaction at positions 2 and 3 is so complete that there is never any substitution at both of these positions in one glucose unit, $k_a = k_b = 0$ and $M + N = 1$.

In using these equations, it should be remembered that t is not proportional to time unless all conditions remain constant during the reaction. Rather, t is to be considered as a parameter which includes a time factor, by means of which corresponding values of S and the individual types of substituted glucose units may be calculated.

Similar equations may be calculated for the case where the extent of reaction is governed by equilibrium constants rather than rate constants. These equations have been published[6] for the important case where there is no mutual interference between substituents in positions 2 and 3, and will not be repeated here. The distribution curves are identical for rate-controlled and equilibrium-controlled distributions if all three hydroxyls have equal reactivity. If the reactivities are different, the distributions are similar for the two cases. It should be noted, however, that with equilibrium control the maximum of any monosubstituted species (s_2, s_3, or s_6) will occur at an average substitution $S = 1$, and of a disubstituted species at $S = 2$. This is not true for rate-controlled reactions unless either the reaction rate constants are all equal or $k_a = k_b = 0$.

In order to visualize the implications of the distribution equations, it is helpful to compare calculated plots for several assumed ratios of reactivities. In Figure 1, the fractions of the anhydroglucose units present in the unsubstituted, monosubstituted, disubstituted, and trisubstituted forms are plotted against the total substitution, S, for several assumed ratios of equilibrium and reaction rate constants and with the further assumption of no mutual interference between positions 2 and 3. One important point is immediately apparent from Figure 1. There is not a great deal of difference among the curves for a given value of c, in spite of fairly wide differences of reactivity that were assumed. It is hardly likely that analytical methods for the quantities plotted in Figure 1 will ever be good enough to allow valid conclusions to be drawn about the relative reactivities of the three sorts of hydroxyls. It is even less to be expected that such determinations will allow the accurate comparison of the uniformity of two different samples of the same degree of substitution. As a matter of fact, most of the data obtained by investigators who determined only the amount of mono-, di-, and tri-substituted anhydroglucose units present in uniform

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[6] H. M. Spurlin, *J. Am. Chem. Soc.*, **61**, 2222 (1939)

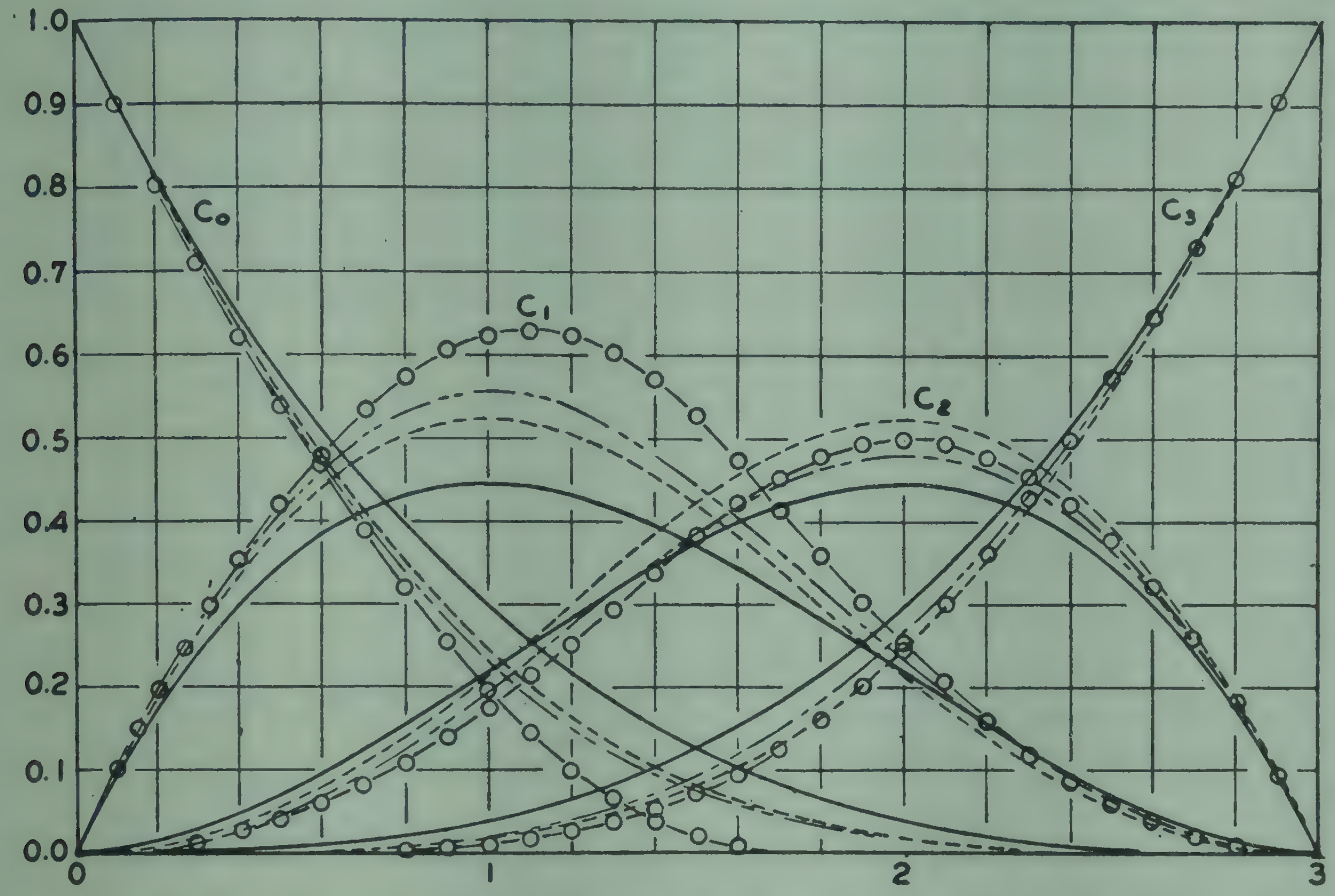

Fig. 1. Theoretical over-all distribution of substituent groups in cellulose (Spurlin[6]).

Abscissa: Average number of substituents per anhydroglucose unit.
Ordinate: Fraction of total number of anhydroglucose units substituted as indicated.

c_0, unsubstituted; s_0
c_1, monosubstituted; $s_2 + s_3 + s_0$
Ratio of equilibrium constants:
——— 1:1:1
- - - - - - 1:4:16
——— - - 1:1:10

c_2, disubstituted; $s_{2,3} + s_{2,6} + s_{3,6}$
c_3, trisubstituted; s_3
Ratio of rate constants:
——— 1:1:1
—○— 1:1:10

derivatives can be correlated within experimental error by the assumption that all three sorts of hydroxyls have the same reactivity[6] with no interference between positions 2 and 3. Such interference actually occurs in many cases, as will be discussed below.

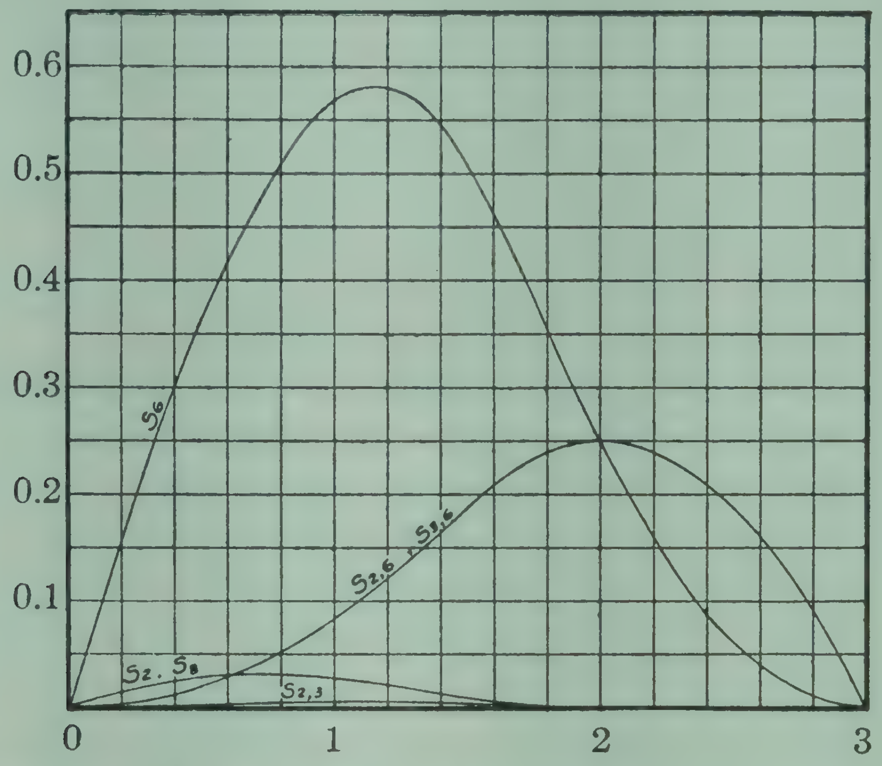

Fig. 2. Proportions of the six different mono- or di-substituted glucoses, if the nature of substitution is determined by the rates of reaction of the three hydroxyls in the ratio 1:1:10 (Spurlin[6]).

Abscissa: Average number of substituents per anhydroglucose unit.

Ordinate: Fraction of total number of anhydroglucose units substituted as indicated.

$s_{2,3}$, $s_{2,6}$, $s_{3,6}$ = fraction of anhydroglucose units with two substituents, in 2,3-, 2,6-, or 3,6-positions.

s_2, s_3, s_6 = fraction of anhydroglucose units with one substituent, in 2-, 3-, or 6-position.

The relative reactivities of the three sorts of hydroxyls may be determined with reasonable precision if all eight possible manners of substitution of the anhydroglucose units are measured separately. That this is so is indicated in Figure 2. As is evident, a tenfold greater reactivity of the primary hydroxyl than either of the two secondary hydroxyls is readily detected by comparing the ratio of s_6 to s_2 or s_3 at a substitution of 0.5–1.0, or of $s_{2,6}$ or $s_{3,6}$ to $s_{2,3}$ at a substitution of 1.5–2.0. The determination of reactivity ratios under conditions of uniform reaction, as in solution, is at present in a satisfactory condition, and will be reviewed below.

It would be desirable to be able to use the available information about reactivity ratios to evaluate the uniformity of cellulose derivatives by analysis for the different types of substitution. By comparison of these results with the theoretical distribution, a quantitative evaluation of uniformity could be obtained.

Unfortunately, it is still not possible to specify methods for the exact quantitative evaluation of uniformity by using these principles. The difficulty is twofold. To begin with, it is apparent from Figure 2 that the curves have rather flat shapes in the regions where content of a given species is appreciable. Accordingly, a mixture of material of, say, D.S. 0.8 and 1.2 would be hardly distinguishable from a uniform material of D.S. 1 if only the six quantities in Figure 2 were determined.

It turns out that the detection of nonuniformity depends on exact analysis for species that would be present in small quantity in a uniform product. For example, the amount of unsubstituted glucose in a product of D.S. 2.5 is a good criterion of the uniformity.

The other important difficulty in a statistical study of the evaluation of uniformity of the substituted glucose content arises from the breakdown of the assumptions involved in the calculations. It is becoming increasingly apparent that interference between positions 2 and 3 is an important factor in rate-controlled reactions.[7] This necessitates the use of the complete mathematics of equations 3–11 which has never been done over a wide enough range of D.S. to allow the evaluation of k_a and k_b. Another complication arises if the ratio of reactivities changes during reaction. For example, in etherification to a high D.S., there is a profound change in the nature of the medium surrounding the individual hydroxyl groups from the initially hydrophilic alkali cellulose to the hydrophobic ether. It would hardly be surprising if there was a change in the reactivity ratios as a consequence of the change of medium. The mathematical difficulties of handling such a situation would not be insuperable, but there appears to be little chance that the necessary precise data will be obtainable.

As a consequence of the above difficulties, it is scarcely surprising that, in industry, the evaluation of uniformity is on a purely empirical physical basis, depending on strict specifications of turbidity in solution, solubility range, viscosity–concentration behavior, and the like. It must not be supposed, however, that the effort that has been expended in the study of the statistics of substitution reactions has been wasted. Many erroneous notions have been dispelled. Above all, a very good idea of that which is practically attainable has been reached during the last twelve years.

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[7] T. E. Timell and H. M. Spurlin, *Svensk Papperstidn.*, **55**, 700 (1952).

(b) EXPERIMENTAL EVALUATION OF DISTRIBUTION THEORY

The most important use of the calculated distribution curves is to serve as a logical framework for the correlation of experimental results on the nature of partially substituted derivatives. The experimental work usually has purposes other than mere confirmation of the equations. The most frequent objective has been to study the availability of fibrous cellulose for reaction. There has also been important work on the directing influence of specific reaction conditions, such as etherification of the association complex of cellulose with sodium and cupric hydroxides (see Table 15, Section E of this Chapter IX). There has, however, been enough work to furnish experimental confirmation for the statistical theory of the arrangement of substituents in cellulose derivatives.

A complete confirmation of the theory would require a study of the influence of the state of substitution of one anhydroglucose unit on that of its neighbors. Because of the experimental difficulty of such an approach, attention has been confined up to the present to the following alternative methods.

In the first method, a series of derivatives of increasing substitution is prepared, and the amount of some specific type of substitution is determined. For example, the amount of primary substitution may be estimated by the techniques of tritylation,[8] tosylation–iodination,[9,10] rate of tosylation.[11] In addition, the amount of unsubstituted glycol groups in the 2,3- positions (i.e., the glycol number) can be estimated by cleavage by periodate[12] or lead tetraacetate.[12] Because of the limited amount of information obtainable by these methods, this type of approach cannot be expected to give a completely satisfactory confirmation of the theory. However, it is satisfying to know that results so far obtained by these methods on uniform products are in agreement with the theory.

In the second method of approach, an attempt is made to determine the number of anhydroglucose units substituted in each of the eight possible manners for a series of derivatives of increasing total substitution. Unfortunately, this method is applicable only to cellulose ethers, since the available methods of analysis depend on hydrolysis to the monomeric substituted glucose stage without the loss of substituents which occurs on hydrolysis of other derivatives. Of course, analytical information on the hydrolyzed products can be supplemented with information of the first kind, such as the glycol number of the unhydrolyzed material.

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[8] I. Sakurada and T. Kitabatake, *J. Soc. Chem. Ind., Japan*, **37**, Suppl. binding, 604 (1934).

[9] C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Am. Chem. Soc.*, **70**, 2740 (1948).

[10] F. B. Cramer and C. B. Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939).

[11] T. S. Gardner and C. B. Purves, *J. Am. Chem. Soc:*, **64**, 1539 (1942).

[12] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942).

[13] H. H. Brownell, Thesis, McGill Univ., Montreal, 1953.

It would be especially desirable to isolate, characterize, and weigh the eight types of substituted glucose, rather than to depend on frequently rather indirect analytical methods. With the present highly developed status of paper chromatography, countercurrent distribution between solvents, and high-vacuum distillation methods, such an approach should not be too difficult. It is encouraging to note that even in the complicated case of hydrolyzed hydroxyethyl cellulose, it was possible by the use of paper chromatography to resolve all the glucose substitution types except those substituted in the 2- position from those substituted in the 3- position.[13] The early attempts by Traube and his coworkers[14,15] to separate the methylated glucoses by distillation were not so successful, though resolution of unsubstituted, mono-, di-, and tri-substituted glucoses was reasonably complete even without the use of a distillation column.

By selecting from the methods outlined above and when necessary developing new methods, Timell[5,16–19] succeeded in establishing that the statistical theory of distribution of substituents does indeed hold for reasonably uniform ethers (see Table 17, Section E of this Chapter IX). In the case of methyl cellulose, the reactivities of the three sorts of hydroxyls did not appear to differ by factors of more than 2:1 when either solutions of cellulose in quaternary bases or fibrous alkali cellulose were reacted with methyl sulfate or methyl chloride. On the other hand, in the presence of excess cupric hydroxide, alkylation in the primary position is suppressed (Table 15, IX-E).

As had been expected by earlier investigators, the presence of ionized substituents in either secondary position greatly reduces the ease of introduction of a second ionized substituent in the adjoining secondary position.[7] In fact, with carboxymethyl celluloses of D.S. 1 or less, there was no evidence for substitution in both secondary positions at the same time, and the mathematics of equations 3–11 with $k_a = k_b = 0$ appeared to apply. This conclusion cannot be strictly true, since by the use of drastic reaction

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[14] A. Funk, Dissertation, Berlin, 1935; H. J. Schenck, Dissertation, Berlin, 1936.

[15] W. Traube, R. Piwonka, and A. Funk, *Ber.*, **69B**, 1483 (1936).

[16] T. E. Timell, *Svensk Kem. Tid.*, **62**, 49, 129 (1950).

[17] T. E. Timell, *Svensk Paperstidn.*, **55**, 649 (1952).

[18] T. E. Timell, *Svensk Paperstidn.*, **56**, 311 (1953).

[19] T. E. Timell, *Svensk Paperstidn.*, **56**, 483 (1953).

conditions it is possible to prepare carboxymethyl cellulose of substitution greater than 2.

As a result of Timell's thorough investigations, there can remain no doubt about the usefulness of statistical considerations as a guide to the study of the manner of arrangement of ether substituents along the cellulose chain. Furthermore, it is interesting to note that under usual technical conditions of etherification, the initial reactivities of the three sorts of hydroxyl groups are rather close to one another. This is particularly true of the 2- and 6- positions, the reactivity in the 3- position being uniformly somewhat lower.[5]

It is also becoming increasingly apparent that the original supposition[6] is correct that there is frequently marked interference between reaction at positions 2 and 3. Although so far firmly established only in the case of the carboxymethyl group, similar effects may be expected in all cases in which ionized or bulky substituents are involved. It may be anticipated that tosyl, trityl, and benzyl groups will give large mutual interference. The presence of even a relatively small adjacent group, such as ethyl or acetyl, would be expected to reduce the rate of introduction of tosyl or trityl groups into the adjoining positions.

This mutual interference does not in any way invalidate the statistical treatment. It simply necessitates the determination of more reaction rate constants in order to specify the nature of the system. For example, if the rate of tosylation is to yield information about the amount of substitution of each sort of hydroxyl in cellulose acetate, it will be desirable to consider the following seven rate constants: one constant for the primary group; three constants for position 2, depending on whether position 3 is unsubstituted, carries an acetyl group, or carries a tosyl group; and three similar constants for position 3.

(c) UNIFORMITY OF METHYL CELLULOSE

The application of the concept of statistical distribution of substituents to the evaluation of uniformity may be illustrated by the comparison of the nature of methyl celluloses prepared in different manners. The question is important because some of the conclusions that are drawn, even in the current literature,[20] are not reconcilable with the principles adopted in this book.

The principal point at issue is the nature of cellulose xanthate in solution (Section F of this Chapter IX and Chapter X-C). By reaction of this solution with diazomethane generated *in situ*, Lieser[21] obtained methyl celluloses of D.S. about 0.5. It is not very probable that the methyl groups were introduced solely in the positions originally occupied by xanthate groups.[22] The following arguments apply only to the uniformity of the methyl celluloses. These, when subjected to acetolysis at low temperature with a mixture of acetic anhydride, acetic acid, and sulfuric acid, gave cellobiose octaacetate in yields of 11–14 g. per 100 g. of methyl cellulose used. Similar experiments with unmethylated cellulose gave yields of 46%.

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[20] T. Lieser, *Kurzes Lehrbuch der Cellulosechemie,* Bornträger, Berlin, 1953.

These experiments prove that the methyl cellulose samples contained many of their anhydroglucose units unsubstituted and adjacent in pairs. Further conclusions that can be drawn from these results depend on what assumptions are made. Lieser assumed that a methyl cellulose of D.S. 0.5 would not contain more than one substituent on any individual anhydroglucose unit, and that the yields from methyl cellulose should be corrected by a factor corresponding to the yield from cellulose (i.e., 46% for these experiments). He further assumed, without carrying out the necessary calculations, that the observed yields could not be explained on the basis of random arrangement of the substituted anhydroglucose units. Lieser therefore concluded that the cellulose in viscose is only 50% available for reaction, and that the samples consisted of mixtures of monomethyl cellulose and unaltered cellulose. This conclusion is unjustified, as was pointed out in the first edition of this book as well as by Staudinger and Zapf[23] and by Timell.[5] Obviously, more than half of the anhydroglucose units of a methyl cellulose of D.S. 0.5 would be unsubstituted. As is evident from Figure 1, the content of unsubstituted anhydroglucose units for D.S. 0.5 can go as high as 57.8% if all hydroxyls have equal availability. There would be a better than 25% chance that any cellobiose unit that was formed by hydrolysis would be unsubstituted. The observed yields of cellobiose octaacetate (about 25% of that from cellulose) are thus in excellent agreement with those to be expected on the basis of a perfectly uniform methyl cellulose.

There is a further point that needs attention in this connection. The assumption is implicit in the above reasoning that the rate of hydrolysis of the 1,4-glucosidic bonds in the chain structure will not depend on the state of substitution of the adjoining anhydroglucose units. This assumption is far from being justified. Lieser[21,24] recognized that methyl celluloses undergo the acetolysis reaction more rapidly than does cellulose, and that incompletely reacted products isolated from the reaction mixture were lower in methoxyl content than was the starting material. During the acetolysis reaction, a mixed acetate–methyl ether is being degraded. It is now known (see Section G of this Chapter IX) that cellulose ethers undergo acid degradation more rapidly than does cellulose acetate. It may therefore be expected that the methyl-substituted portions of a mixed acetate–methyl ether will be hydrolyzed preferentially. This will lead to an increased chance that any remaining dimer unit will be substituted only with acetyl groups, and will enhance the yield of cellobiose octaacetate above that to be expected on comparison with cellulose itself, for which the theoretical yield is only 67 mole per cent,[25] even if all cellobiose units, once they are formed, are protected from further degradation.

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[21] T. Lieser, *Ann.*, **483**, 132 (1930).

[22] Chian-Yuang Chen, Ralph E. Montonna, and C. S. Grove, Jr., *Tappi*, **34**, 420 (1951).

[23] H. Staudinger and F. Zapf, *J. prakt. Chem.*, **156**, 261 (1940).

TABLE 1

Acetolysis of Cellulose and Methyl Cellulose
(From data of Lieser and Jaks[21,24])

Type of product	D.S.	Cellobiose content calculated, mole per cent	Cellobiose octaacetate isolated, g./100 g. of methyl cellulose	Cellobiose octaacetate yield, calculated, g./100 g. of methyl cellulose[a]
Fibrous cellulose	0	100	45	—
Fibrous methyl cellulose[b]	0.28	54	37	23
	0.46	36	23	15
	0.65	22	22	10
	0.73	17	26	8
	0.74	17	19	8
	1.26	3.5	14	1.5
Technical methyl cellulose[c]	>1.5	<0.2	0	<0.1
Methyl cellulose from xanthate[d]	0.50	32	11	14
	0.46	36	14	15

[a] Based on a 45% yield from the cellobiose content for fibrous products,[24] 46% for xanthate.[21]
[b] Prepared by reaction of cellulose with methyl sulfate in the presence of 20% NaOH.
[c] "Tylose," presumably prepared with methyl chloride and 35% NaOH.
[d] Prepared by reaction of diazomethane with viscose solution.

In spite of the uncertainty arising from the above considerations, acetolysis is a potentially valuable tool for the evaluation of the uniformity of cellulose ethers. As was pointed out above, it is desirable for this purpose to use a method for the determination of some constituent that would be present in very small quantity in a uniform product. Above a D.S. of 1, the content of unsubstituted cellobiose units fulfills this requirement admirably. It is therefore interesting to compare with the theory for a uniform product some yields of cellobiose octaacetate obtained by Lieser and Jaks[24] from methyl celluloses obtained by reaction of fibrous cellulose with methyl sulfate in the presence of 20% NaOH. These data are given in Table 1, together with comparable data for cellulose, a technical water-soluble methyl cellulose, and the previously mentioned methyl cellulose samples prepared from cellulose xanthate. It is immediately apparent from these results that the yields of cellobiose octaacetate from the fibrous products prepared with 20% NaOH were higher than could have been expected from a uniform product. The technical product and the ethers prepared from xanthate gave yields in very good accordance with the theory for a uniform product. These differences are in agreement with general experience. The technical products, prepared with strong NaOH and methyl chloride, are much more uniform than are ethers prepared with methyl sulfate and weak NaOH (see Section E of this Chapter IX). The product prepared in solution from the xanthate would be expected to be uniform.

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[24] T. Lieser and R. Jaks, *Ann.*, **548,** 204 (1941).
[25] W. Kuhn, *Ber.*, **63B,** 1503 (1930).

On the basis of these results, the acetolysis method would be expected to be especially suited to the evaluation of uniformity of technical products in the substitution range 0.7–1.2.

(d) COMBINED RATE AND EQUILIBRIUM CONTROL

Until recently, very little progress had been made in the study of the distribution of substituents in cellulose esters. This is, of course, a difficult field because of the ease of removal and migration of ester groups. To be sure, previous investigators[8,9,11] had shown that the secondary cellulose acetates of commerce had roughly equal amounts of hydroxyl content in the primary and secondary positions. The situation has now been largely clarified by the efforts of Hiller[26] and Malm and coworkers.[3,27–29] These workers found that the normal secondary cellulose acetate of commerce (D.S. 2.3–2.4), when dissolved in acetic acid containing 2–3% water, would initially increase slightly in substitution and then gradually decrease. With products of lower substitution (D.S. 1.7), the initial rise in substitution was much more pronounced. This behavior is illustrated in Figure 3 for three samples of cellulose acetate. The sulfuric acid used as a catalyst in this case did not change the general nature of the results, though the higher temperatures necessary to secure acceptable reaction rates in the absence of catalyst decreased the initial rise. It was clear to both sets of workers that the explanation of this behavior was simple. The free primary hydroxyl content of the sample was initially greater than that corresponding to equilibrium with the acetic acid–water mixture used, and these primary hydroxyls were acetylated fairly rapidly, resulting in a tendency for the substitution to rise. At the same time, the content of free secondary hydroxyl was initially lower than the equilibrium value, so that deacetylation occurred in these positions, but at a lower rate than the initial acetylation in the primary position. As the more rapid reaction in the primary position approached equilibrium the continuing hydrolysis in the secondary positions became dominant. The validity of these conclusions was checked by tritylation experiments. It was also found by Malm[29] that the rate of the acid-catalyzed acetylation by acetic anhydride was more rapid in the primary position than in the secondary positions. Furthermore, there was a good correlation of optical rotation

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[26] L. A. Hiller, Jr., *J. Polymer Sci.*, **10**, 385 (1953).

[27] C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Am. Chem. Soc.*, **70**, 2740 (1948).

[28] C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Am. Chem. Soc.*, **72**, 2674 (1950).

[29] C. J. Malm, L. J. Tanghe, B. C. Laird, and G. D. Smith, *J. Am. Chem. Soc.*, **74**, 4105 (1952).

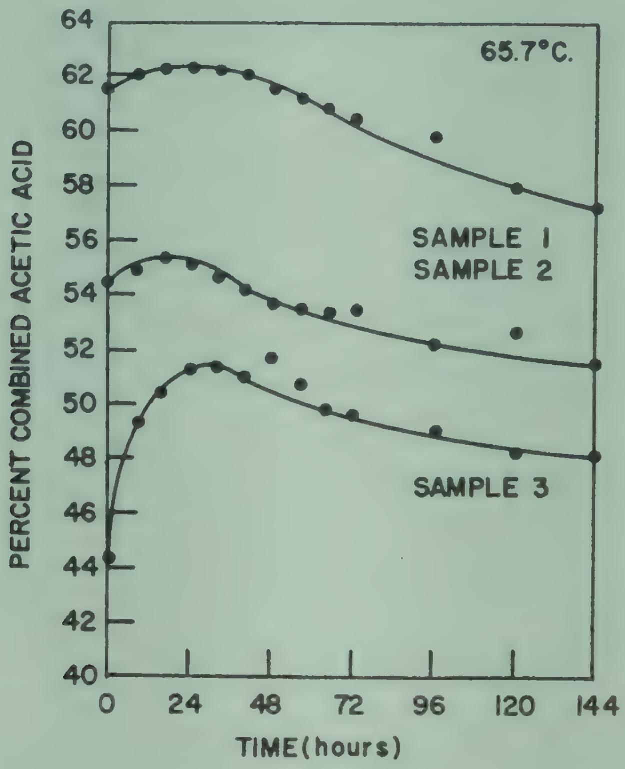

Fig. 3. Acid-catalyzed reaction of secondary cellulose acetates with 97.2% acetic acid (Hiller[26]). Concentration of H_2SO_4, 0.1%; temperature, 65.7°C.

with the relative amount of free primary and secondary hydroxyls, allowing the redistribution reaction to be followed readily.

Hiller[26] undertook a very elaborate mathematical analysis of his rate data, with the objective of calculating the pertinent rate and equilibrium constants. He was unable to segregate the effects of reaction at the two secondary positions, and therefore based his calculations on the questionable assumption that the rates in the secondary positions could be characterized by a single constant. This is a fairly serious drawback of those portions of his calculations based on observations after long elapsed times, and particularly of his estimates of the equilibrium constants for reaction in the secondary positions. However, his results should prove of great value in the interpretation of the commercial process of hydrolysis of cellulose triacetate to secure uniform products of lower substitution. Hiller's values of rate constants are given in Table 2 and the equilibrium constants are shown in Figure 4 as a function of temperature. The net result of the interaction of the rate and equilibrium constants is that in a given acetic acid–water mixture, the equilibrium extent of acetylation of the primary hydroxyls tends to be high, and the rate of attainment of this equilibrium is relatively high. Conversely, with the secondary hydroxyls the equilibrium substitution is low, as is the rate of attainment.

TABLE 2

Rate Constants for Acetylation of Cellulose (Hiller[26])

	Rate constant × 10^3, mole^{-1} hr.$^{-1}$			
	Primary groups		Secondary groups	
Temperature, ° C.	Acetylation	Deacetylation	Acetylation	Deacetylation
	Uncatalyzed reaction			
84.4	2.6 ± 1.8	1.9	0.74	0.057
94.2	6.5 ± 3.0	3.6	1.7	0.15
104.4	9.2 ± 3.0	4.9	3.6	0.40
115.1	14.8 ± 6.0	7.4	7.6	0.94
	Acid-catalyzed reaction (0.1% H_2SO_4)			
46.0	1.5 ± 0.2	2.5	0.92	0.035
54.8	3.8 ± 1.8	4.7	1.3	0.060
65.7	6.3 ± 1.0	6.3	2.0	0.12

In commercial practice, the hydrolysis of primary cellulose acetate is carried out in the presence of so much water that the equilibrium substitution would be very low for both primary and secondary hydroxyls. As a consequence, the reaction is largely rate controlled, and the primary hydroxyl content is considerably higher than the equilibrium value. This has important consequences, since a high ratio of free primary to secondary hydroxyl in cellulose acetate results in a wider range of solubility than the converse situation. A similar situation is encountered with ethyl cellulose of low D.S.; the product substituted only in the secondary positions, prepared in the NaOH–Cu(OH)$_2$ system, is more soluble in water than the usual product prepared in the absence of copper.[15]

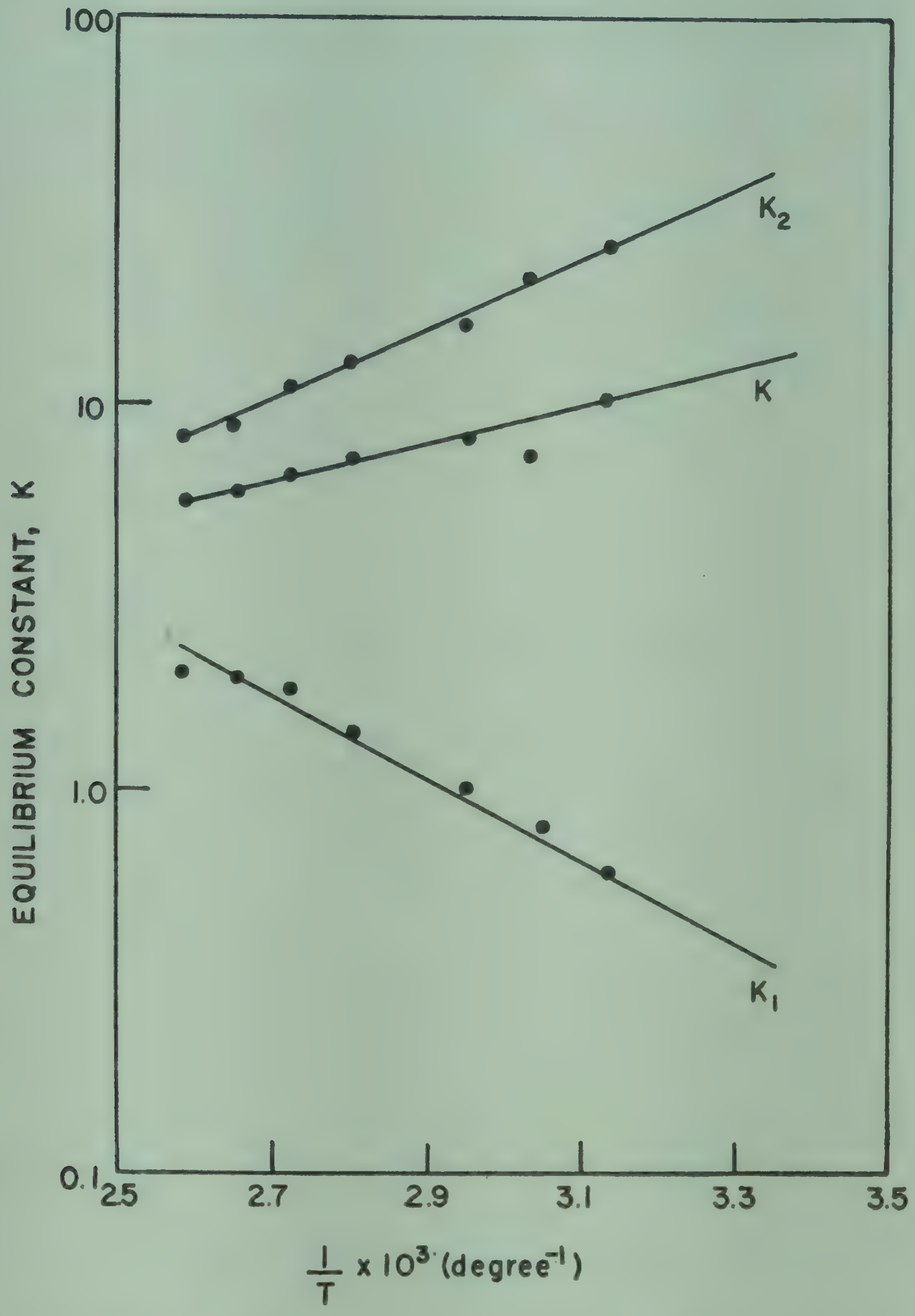

Fig. 4. Temperature dependence of equilibrium constants for hydrolysis of cellulose acetate (Hiller[26]). K_1 is equilibrium constant for hydrolysis of primary hydroxyls; K_2, for secondary hydroxyls; K, for over-all reaction.

In addition to his studies of rates and equilibrium of acetylation, Hiller[26] also determined the rate of degradation of his samples. This facet of his work will be treated in more detail in Section G of this Chapter IX. The result of paramount importance in connection with this discussion is the fact that even under the most favorable conditions of low temperature and high catalyst concentration, the rate of degradation is so high that equilibrium cannot be approached closely without excessive degradation. It is therefore clear that a uniform cellulose acetate of D.S. 2.0–2.5 and of acceptably high degree of polymerization (D.P.) will never be secured by reaction of a nonuniform product with acetic acid–water mixtures until the equilibrium is closely approached. This conclusion is especially true for the direct acid-catalyzed esterification of fibrous cellulose. For this reason the commercial process involves acetylation nearly to the triacetate, which must then be uniform. This product can then be hydrolyzed in solution to give a uniform secondary acetate.

2. Reaction of Cellulose Fibers

The raw material for the preparation of cellulose derivatives is nearly always fibrous cellulose derived from plant sources. However, a large fraction of the cellulosic material in these native fibers is crystalline in nature (see discussion of fiber structure in Chapter IV-B), and the interior of the crystalline regions is inaccessible to chemical reagents as long as this native crystalline structure is maintained. All reactions of the crystalline region have to start at the surface and proceed gradually inward. It has long been apparent that this inaccessibility of a portion of the cellulose hinders a uniform reaction. Means for overcoming this tendency toward nonuniformity constitute a large portion of the technology of cellulose reactions. The situation may be much more serious than mere nonuniformity of the product; cellulose may not react at all or only with extreme difficulty in a reaction that proceeds nicely with low molecular weight compounds. Therefore, the *rate of reaction* of cellulose as well as the *uniformity of reaction* must be considered. In addition, the possibility of conditions promoting serious degradation always exists.

The difficulties of rate and uniformity of reaction of fibrous cellulose are due, beyond a shadow of a doubt, to the difficulty of getting the reagents to the cellulose hydroxyls. In order to point out the nature of the stages of difficulty that are encountered, a simplified résumé of some of the details of fiber structure discussed in Chapter IV will be presented.

(a) FIBRILLAR STRUCTURE OF NATIVE CELLULOSE

The basic unit of organization of native cellulose, whether fiber, membrane (*Valonia*), or unorganized products such as bacterial cellulose, is a fibril about 100 A. in diameter and of great but indefinite length.

As was mentioned in Chapter IV-B, the current theories of cellulose fiber reactivity do not take the fibrillar structure into account. Some of them are even incompatible with the idea of discrete fibrils. In the following discussion, an attempt will be made to show that the peculiarities of cellulose reactions are easily explained on the basis of behavior of and interactions of fibrils.

The literature of cellulose reactions contains many designations founded on preconceived ideas of mechanism or else designed to conceal ignorance. Among these terms are microheterogeneous and macroheterogeneous reaction, micellar surface reaction, permutoid or quasihomogeneous reaction. Since cellulose reactions are not as clean-cut as these terms would indicate, and in any case terminology does not assist in understanding, no further use of these designations will be made in this Section.

Each fibril behaves as if it were largely crystalline in its core, with the degree and perfection of organization decreasing as the surface is approached. There is no evidence at all for a separate, amorphous phase or cementing material holding the fibrils together in fibers of purified native cellulose. The bonding between fibrils in fibers appears to be due to the same factors that operate in bonding fibers to make paper (Chapter VIII). The bonding in paper seems to be due to several factors. The surface area of the fiber is increased by tearing and splintering. The newly created surfaces are swollen by water and made easily deformable. When these surfaces are dried in contact with each other, strong bonds allied in character to the formation of interpenetrating crystalline regions are formed. It is especially characteristic that these bonds between fibers are preserved when the paper is nitrated or acetylated. In the same manner, a fiber can preserve its identity when transformed into a derivative. This analogy furnishes good evidence that cellulosic surfaces created in the presence of water will adhere strongly when dried in contact.

In the water-swollen state during growth of the fibers, crystallization is not complete although the cellulose molecules must be largely oriented in the direction of the axis of the fibril.[30] In this condition the fibrils will be easily deformable and will therefore pack fairly closely in the fiber. As water is withdrawn by growth processes or drying, crystallization in the fibril will occur. It is plausible to postulate that occasionally this crystal growth process will occur in such a fashion that it can cross over into an adjacent fibril, thus forming a very strong bond between fibrils. More often, the structure will remain disorganized at the interface between fibrils and there will remain a surface of weakness. The degree of interfibrillar crystallization may well be an important factor in the phenomenon of "hornification" (very poor reactivity) referred to later. For the present discussion, it will be assumed that a normally reactive cellulose sample is being considered, and that the bonding between fibrils is loose.

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[30] E. E. Berkley and T. Kerr, *Ind. Eng. Chem.*, **38**, 304 (1946).

The fibrillar structure of the fiber enables distinguishing three stages of penetration of reagents. (1) The fiber with a diameter of about 100,000 A., may react only on the surface. (2) The surface of the fibril, with a diameter of 100 A., may be available for reaction. (3) The cellulose molecule, with a diameter of less than 10 A., may be freely accessible to the reagents. On the basis of these considerations alone, it is evident how much can be gained if reagents can penetrate the fiber. A thousandfold decrease in the time required for reaction would be anticipated if the surface of the crystalline regions could be made freely available, as compared to the time required if a reaction has to work its way inwards from the outer fiber surface. Of course, a further increase in rate would be expected if, by the destruction of the crystalline structure, the individual cellulose molecules could be made available for the reaction from the beginning.

The preceding discussion allows some insight into one of the most important facts of cellulose behavior, that is, that reactivity improves as the degree of swelling in the reaction medium increases, other factors being constant. Since, however, the driving force for the reaction is a function of reagent concentration in the reaction medium, two factors must always be kept in mind. The medium should allow swelling to occur, yet conditions favorable for the chemical reaction in question must be maintained.

That swelling is sufficient to ensure access of reagents to the inside of the fiber is not immediately evident. It might be thought that it would be necessary to have actual capillary channels into the fiber. In capillary channels of a size that would be consistent with other evidence, however, the viscous resistance to actual flow would be enormous and all transfer of reagents would have to be by diffusion. Consequently, all that is involved is the variation of rate of diffusion with the degree of swelling. It has long been known that the rate of diffusion of substances of low molecular weight in dilute solutions or gels of high polymers is very little less than in water,[31,32] in spite of the macroscopic high viscosity of the solution. It is

[31] R. Taft and L. E. Malm, *J. Phys. Chem.*, **43,** 499 (1939).

[32] J. J. Bikerman, *J. Phys. Chem.*, **46,** 724 (1942).

now realized that the local viscosity in a swollen polymer controls the rate of diffusion as well as the flexibility and extensibility of the structure. If swelling has caused the sample to be limp and easily deformable, the rate of diffusion will be high. It is a matter of everyday knowledge that cellulose fibers and films are greatly softened by the uptake of a few per cent of water. The effect of this water of swelling on the rate of diffusion is very pronounced, as may be seen in Table 3.[33,34] A vast amount of experience on the influence of the degree of swelling on the rate of diffusion in polymers indicates that the above behavior may be taken as typical of other swelling agents and other diffusible substances.

TABLE 3

Influence of Swelling on Diffusion of Water Vapor through Cellophane
(From data of Hauser and McLaren,[33] Doty, Aiken, and Mark[34])

Relative humidity, %	Permeability, moles/sq. cm./sec./cm. mercury pressure difference for 1-cm. thickness
100	2700×10^{-13}
50	300
0	1.5

Some speculation is in order about the details of the swelling mechanism of native fibers, particularly with agents such as water and pyridine, which open up the interior of the fiber without noticeable attack on the crystalline regions. It is probable that the outer wrapping layers of the fibers, which interfere very markedly with the action of strong swelling agents (Chapter IV-B), are not important in the case of the limited swelling possible with water, pyridine, or acetic acid. After all, the fiber was more highly swollen when originally laid down, and the wrapping layers had to be able to accommodate the corresponding degree of swelling. It is thus probable that the outer portion of each fibril throughout the fiber swells slightly, causing the fiber as a whole to expand; at the same time the fiber loses some of its flattened shape and becomes more cylindrical. There will then be an intercommunicating network of swollen material, allowing ready diffusion of reagents into the fiber.

Inspection of electron micrographs of clumps of fibrils in cotton fiber disintegrated under water gives the impression that the fibrils have enough elasticity to spring apart under swelling conditions and thus create actual voids in the structure (Chapter IV-C). Such an interpretation must be viewed with caution, since these observations were made on samples redried without the constraints present in the intact fiber. However, the ease of splitting along the fibrillar interfaces demonstrated by the electron micrographs certainly proves that lateral bonding between fibrils is weak in the presence of swelling agents. That actual channels are opened up by the elastic forces between the somewhat disordered fibrils is thus quite plausible. It must be emphasized, however, that these channels are probably not intercommunicating and certainly do not occupy a large fraction of the increase of volume of the fiber that is observed on swelling. Also, fibers such as ramie show no evidence of channels between fibrils, yet ramie with its beautifully parallel fibrils is nearly as reactive as cotton or wood pulp with a more irregular structure (see Fig. 49, Chapter IV-C). It is therefore very probable that most of the transfer of reagents in swollen fibers is through a zone of swollen material surrounding the fibrils, rather than primarily through empty channels.

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[33] P. M. Hauser and A. D. McLaren, *Ind. Eng. Chem.*, **40,** 112 (1948).

[34] P. M. Doty, W. H. Aiken, and H. Mark, *Ind. Eng. Chem., Anal. Ed.*, **16,** 686 (1944).

(b) VARIATION OF REACTIVITY OF CELLULOSE

The above concept of interfibrillar swelling has been discussed in detail to help explain the very wide variation in the reactivity of different cellulose samples. This variation is particularly evident in reactions such as acetylation, where the swelling power of the medium is necessarily limited by the lack of technically suitable chemically inert swelling agents. The reactivity of different samples of cellulose in such cases can range from very good to very poor. In cases of poorly reactive cellulose samples, reaction is always observed to be largely confined to the surface of the fiber. If drastic conditions or very long times are used, the whole fiber will, of course, eventually react. The difficulty here is that those portions of the fiber that react first are subjected to the full degrading action of the medium for a long time, and the final product will be too low in D.P. to be useful. It is therefore desirable to use cellulose of high reactivity, even in cases where a long reaction time would be economically feasible.

From experimental evidence, much of the observed difficulty with poor reactivity can be traced to a decrease in the reactivity of initially reactive cellulose, that is, the hornification referred to previously. If, for example, a water-wet sample of reactive cellulose is dried slowly at 100°C., there will be a pronounced drop of reactivity as measured under normal acetylating conditions. The effect is much more pronounced if the cellulose is first swollen in aqueous NaOH, water-washed, and then dried hot.

The opinion seems to be gaining ground that this loss of reactivity is due to an effective cross-linking of the cellulose, which reduces or even completely inhibits the ability of the fiber to swell in usual acetylation baths. There have been numerous proposals of actual chemical cross-linking, but there seems to be no necessity to invoke such action. The possibility of crystal growth between fibrils appears to be an adequate explanation The conditions of heat and moisture that lead to hornification are also those that promote crystallization of cellulose. Another indication that partial cross-linking of fibrils by crystallization is the correct interpretation is the fact that the effect of hornification is not nearly so pronounced with reaction media, such as NaOH or nitrating baths of high HNO_3 content, which have the ability to penetrate and modify the crystal structure of cellulose.

(c) ENHANCEMENT OF REACTIVITY

The reactivity of fibrous cellulose that has not been subjected to adverse conditions, such as high-temperature drying, is adequate for most purposes. However, much higher reactivity in media of even very poor swelling ability can be obtained if desired. The basis of all pretreatments to enhance reactivity is the great hysteresis of deswelling and crystallization characteristic of cellulose. An example of this hysteresis is the greater moisture content of fibers conditioned to constant humidity from a higher humidity, as compared to conditioning to the same humidity from a dry state (Chapter IV-D). This hysteresis is much more pronounced if the dehydration is carried out from an initially higher degree of swelling than is possible with water alone. The enhancement of reactivity is most effective if dehydration is accomplished by displacement of water by organic solvents. For example, if cellulose is first dissolved in cuprammonium, precipitated in a nearly amorphous state, water-washed, and the water then displaced with organic solvents, a very reactive product is obtained.[35] Acetylation of such an expanded cellulose with pyridine–acetic anhydride mixtures proceeds easily to give a soluble product, whereas native fibers under the same conditions acetylate with difficulty to give insoluble products.[36,37]

One of the most complete studies of the comparative ease of acetylation of cellulose subjected to swelling and then to either vacuum drying or solvent displacement of water from the swollen condition has been carried out by Staudinger and coworkers.[38] These results will be cited in detail in order to give a complete picture of the observed effects. The swelling was brought about by water or by 20% NaOH, as well as by reprecipitation from cuprammonium solution. After thorough water-washing, the swollen samples were either vacuum dried at 40°C. or solvent displaced with acetic acid, pyridine, or methanol followed by benzene. With acetic anhydride–pyridine and cotton at 60°C. the order of decreasing reactivity and, in parentheses, the corresponding acetyl content after 24 hrs., were: (1) reprecipitated, pyridine displaced (27%); (2) mercerized, pyridine displaced (14%); (3) water-swollen, pyridine displaced (8%); (4) water-swollen, dried (5%); (5) mercerized, dried (0.7%). Ramie, linen, and hemp reacted at practically the same rate as cotton. The degree of polymerization also had little influence. All of the above products were nearly completely insoluble in chloroform, showing the absence of a triacetate layer on the surface. The solvent-exchanged samples appeared uniform under microscopic examination.

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[35] P. Karrer, *Einfuhrung in die Chemie der Polymeren Kohlenhydrate*, Akadem. Verlagsgesellschaft, Leipzig, 1925, p. 176.

[36] H. Staudinger and B. Ritzenthaler, *Ber.*, **68B**, 1225 (1935).

[37] H. Staudinger and G. Daumiller, *Ann.*, **529**, 219 (1937).

Similar comparisons were made in another fibrous acetylation process, with H_2SO_4 as catalyst and with benzene in the reaction medium to prevent solution of the product. The mercerized, benzene-displaced sample had an acetyl content of 25% after 1 hr. and 44% (the triacetate) after 24 hrs.; the mercerized, acetic acid-displaced sample, 21% and 44%; the water-swollen, acetic acid-displaced sample, 17% and 42%; the water-swollen, dried sample, 2% for high D.P. and 5% for low D.P. after 24 hrs.; the mercerized and dried sample, 1% after 24 hrs. In most cases, again, the D.P. and fiber type (i.e., ramie, hemp) had little influence. It was further observed that the benzene-displaced samples retained their high reactivity after vacuum drying, and retained 4–8% benzene that could not be removed by vacuum drying alone. The degradation after 24 hrs. acetylation time decreased as the reactivity increased. The superiority of the more reactive samples could doubtless have been much more marked if the comparison of degradation had been made at times required for a given degree of substitution to be reached. It was found that the dried celluloses gave partially substituted products from which most of the acetyl content could be extracted with chloroform as cellulose triacetate. Only a small fraction of the acetyl content of the acetic acid-exchanged products could be removed with chloroform, up to an acetyl content of more than 35%. Beyond this point, the solubility increased rapidly.

Staudinger interpreted his results to mean that all of the cellulose molecules in the solvent-exchanged fibrous products were available for reaction, even in the crystalline regions. So extreme a viewpoint is hardly warranted. In cases discussed below where it is definitely possible for reaction to occur in the crystalline regions, completely soluble products are obtained at intermediate degrees of reaction. This is never possible with cellulose acetate prepared directly from fibrous cellulose. On a submicroscopic scale, there must be discontinuities in reaction during this process.

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[38] H. Staudinger, K.-H. In den Birken, and M. Staudinger, *Makromol. Chem.*, **9**, 148 (1953).

(d) AN INTERPRETATION OF REACTIONS OF NATIVE CELLULOSE FIBERS

A satisfactory interpretation of the observed facts can be built up along the following lines. When fibers that do not swell are reacted, the reaction zone is observed to start in isolated spots at or near the surface of the fiber, and then to spread gradually, leaving cellulose triacetate behind the reaction front.[38,39] All that is necessary is to assume that under conditions of good swelling, everything is displaced in dimensions by a factor of a thousand. The fibril is now exposed to the reagents, and each fibril will begin reacting along its length at isolated spots that either have greater disorder or are more exposed to a direct diffusion path for reagents. In those cases, for example, fibrous acetylation or nitration, where the product crystallizes as its formation is complete, the reaction zone may be pictured as in Figure 5. At an intermediate state of reaction, each fibril may be pictured as having many alternate zones of completely reacted and unreacted cellulose, with cellulose molecules passing between them. Between these zones will be regions of incomplete reaction, which will probably be more swollen than indicated in Figure 5. The swelling of these partially reacted regions may be expected to be much higher than either the reacted or unreacted zones, for the reasons indicated in the discussion of influence of degree of substitution on solubility in Chapter X-A. This swelling will facilitate easy penetration of reagents into the reaction zone. The structure as a whole will be insoluble until the zones of complete reaction have coalesced.

If the medium is a solvent for the product, as in commercial cellulose acetate preparation in contrast to fibrous acetylation, this picture needs to be modified only slightly. In this case, the reacted portions will swell as far as is allowed by the constraints imposed by cellulose molecules penetrating into the unreacted zones. The fiber as a whole will appear under the microscope to swell uniformly as reaction proceeds, but the continuing existence of the fibrils will hold the structure together up to a high extent of reaction. This is exactly what has been observed in many microscopic studies of cellulose acetylation.

[39] K. Kanamaru, *Helv. Chim. Acta*, **17**, 1436 (1934).

There are many observations which support the picture of localized ttack on the cellulose fibril, with the reaction zone then spreading until e whole structure has reacted. When fibers are degraded with acids uner conditions of only slight swelling, they split up into fragments a few undred Angstroms long (Chapter IV, Sections B and C). The same type f fragment can be isolated from esterification reactions, if the conditions are such that the reacted portion of the material is rapidly degraded, thus cutting the interpenetrating molecules which normally hold the unreacted zones together.[40] If, on the contrary, degradation conditions are not severe the few per cent or so of insoluble material remaining near the end of a reaction will consist of gel particles (crystalline fragments surrounded by a swollen mass of reacted material). The extreme behavior is exhibited by fibrous cellulose triacetate of high D.P. prepared under nondegrading reaction conditions. This product is insoluble in the usual triacetate solvents even at very nearly complete reaction. It has been shown by

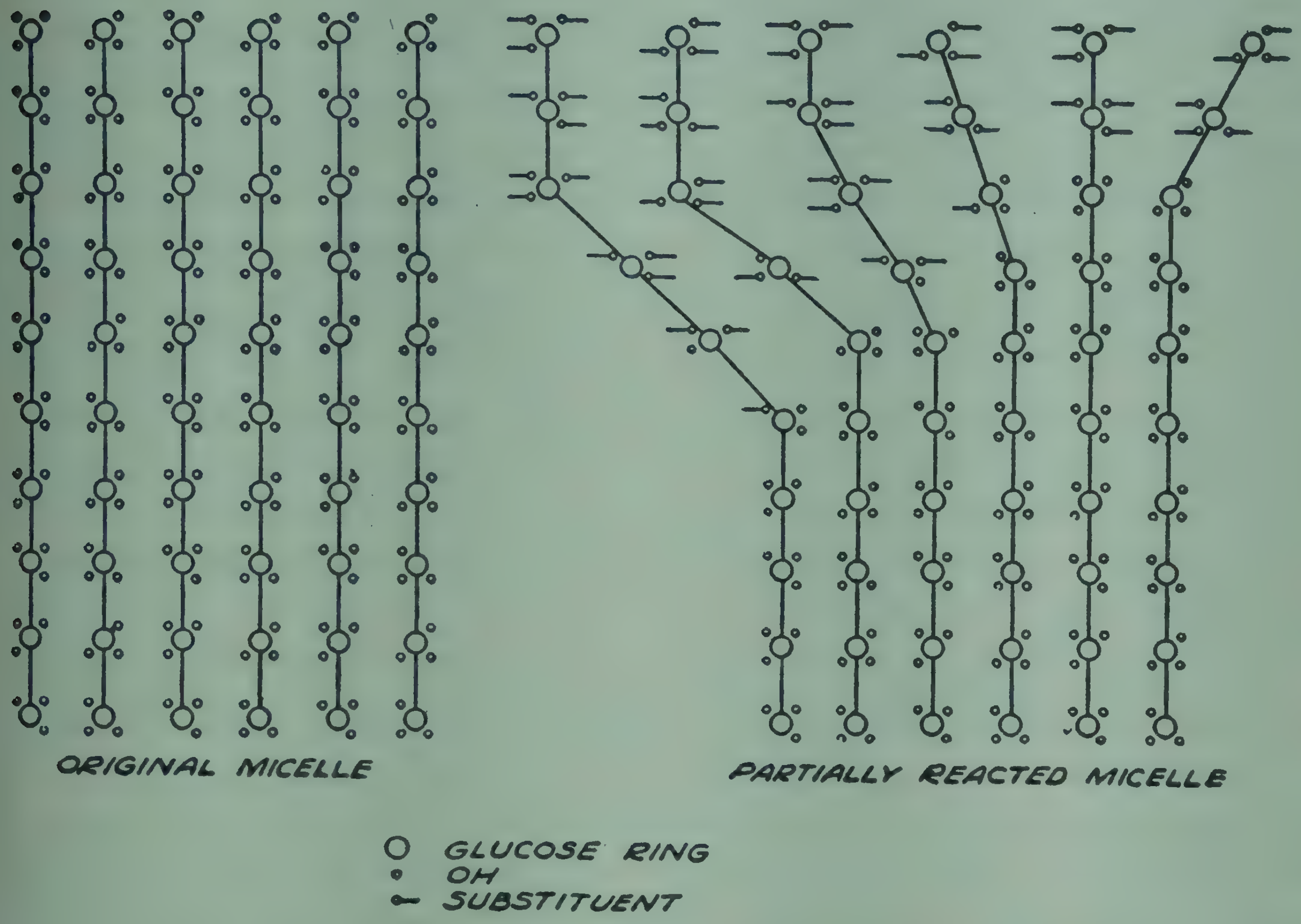

Fig. 5. Reaction zone progressing along crystalline region with retention of fiber structure (Spurlin[1]).

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[40] R. Signer, A. Aeby, F. Opderbeck, and H. Studer, *Monatsh.*, 81, 232 (1950).

Centola[41] that such products still show the x-ray diffraction pattern of cellulose, and apparently even 1% of unreacted cellulose can cause insolubility in such cases.

It may be concluded from the discussion above that in many cellulose reactions the surface of the crystalline region is readily available for reaction, whereas in other cases reaction is primarily from the fiber surface inwards. This is not a matter of mutually exclusive alternatives; rather, all intermediate stages of availability can be expected.

Another point to remember is that the progress of the reaction on the surface of the available regions may impede further reaction. This seldom happens in reactions in organic media, since the reaction products are normally more highly swollen and more compatible with the reagents than is the initial cellulose. However, in the benzylation reaction the initial product is hydrophobic and is not swollen by the alkali which is essential for the further progress of the reaction;[42] the reaction thus becomes more difficult as it proceeds. Another possibility arises when the reaction cross-links the cellulose. For example, the difficulty of reaction of cellulose with more than a few per cent of formaldehyde[43,44] may be due to the progressive cross-linking of the structure, which must impede swelling and diffusion.

There is no evidence for a difference between the inherent reactivity of a crystalline zone of any of the crystalline modifications of cellulose. The differences of reactivity of native fibers, mercerized fibers, and regenerated cellulose can all be explained on the basis of differences in the amount, size, and degree of perfection of the crystalline regions, and on the greater ease of hornification of the more expanded structures when subjected to drastic drying conditions.

(e) REACTIONS OF FIBROUS ADDITION COMPOUNDS OF CELLULOSE

Crystalline addition compounds of cellulose, such as alkali cellulose (Chapters IV-B and IX-D), are uniformly much more reactive than would be expected by comparison with native cellulose. This difference seems to be due to three factors. The media in which the addition compounds are prepared are good swelling agents for cellulose. The crystalline regions are smaller. Most distinctive is the good evidence that reagents can penetrate the crystal lattice of the addition compounds as distinguished from the native cellulose lattice.

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[41] G. Centola, *Atti X° congr. intern. chim.*, **4**, 129 (1939); *Chem. Abstracts*, **34**, 2169 (1940).

[42] E. J. Lorand and E. A. Georgi, *J. Am. Chem. Soc.*, **59**, 1166 (1937).

[43] R. E. Wagner and E. Pacsu, *Textile Research J.*, **22**, 12 (1952).

[44] C. F. Goldthwait, *Textile Research J.*, **21**, 55 (1951).

This last factor has appeared plausible for many years, in order to explain the fact that soluble ethers of low D.S. could be obtained by the reaction of alkali cellulose with etherifying reagents of low molecular weight.[5] The most compelling evidence, however, has come from studies of the reaction of alkali cellulose with CS_2 to form cellulose xanthate.[45,46] (See also Chapter IX-E.) In this reaction, an expansion of the crystal lattice begins as soon as CS_2 absorption starts. The kinetic results support the idea of a uniform reaction throughout the fiber. If the NaOH concentration is below that necessary for mercerization, the course of the reaction is entirely different. An initially rapid reaction slows down very rapidly, so that a final CS_2 uptake of only 30% is found. With NaOH of concentration high enough to transform the crystal lattice of cellulose to alkali cellulose I, the final CS_2 uptake is twice as high. It is probable that with the low concentration of NaOH, reaction was largely confined, under the conditions used, to the more amorphous portions of the cellulose. The above evidence, as well as the evidence from solution properties described in Chapter X-C, leaves no doubt that reaction has occurred, at least to a considerable extent, throughout the fiber if the cellulose has been converted throughout to alkali cellulose.

In general, reactions of alkali cellulose give the most uniform products with the most water-soluble reagents.[5] These would be expected to diffuse rapidly in the hydrophilic alkali cellulose. Thus CS_2 (which possibly forms a water-soluble complex with NaOH[46]), sodium chloroacetate, ethylene oxide, methyl chloride, and methyl sulfate give fairly uniform products in the fibrous reaction. The ethyl celluloses of low substitution are relatively nonuniform. Fibrous products of low substitution obtained with higher alkyl halides are water-insoluble. If, however, the isopropyl ether is prepared in homogeneous medium, it is soluble.

This trend illustrates the fact that despite the availability of the alkali cellulose for reaction, no fibrous reaction product of D.S. less than 3 can be truly uniform unless prepared by an equilibrium reaction. In all fibrous reactions, some of the material must have a different reaction velocity than the rest because of either a difference of diffusion path for reagents or the remaining constraints imposed by the fiber structure. The importance of such constraints is illustrated by the fact that the mercerization reaction itself is hindered by tension or other forces applied to the fiber.

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[45] K. Hess, H. Kiessig, and W. Koblitz, *Z. Elektrochem.*, **55**, 697 (1951).

[46] H. Grotjahn, *Z. Elektrochem.*, **57**, 305 (1953).

It can easily happen that there are local stresses in the fiber that cause a different alkali concentration to be attained in different parts of the fiber. In any case, the crystal lattice forces themselves must cause the available alkali concentration inside a crystalline region to be different from that in more amorphous regions.

When all of these factors are considered, it is surprising that the high-substitution cellulose ethers of commerce are as uniform as they are.[5] Several factors are probably involved in this. One important consideration is that the derivatives pass into solution as the reaction proceeds, so that at least the latter portions of the reaction are under uniform conditions. Another point is the low affinity of partially reacted portions of the product for NaOH; this low affinity will lower the reactivity of these regions in comparison with portions of lower extent of reaction. Finally, it appears to be necessary to invoke the hypothesis of large mutual interference between positions 2 and 3, which will cause the reaction to slow down when a D.S. of 2 is reached in the most reacted portion of the product and allow the remainder to catch up.

3. Chemical Factors Influencing Reactivity

The preceding discussion of reactivity has been from the standpoint of availability of the cellulose hydroxyls for reaction. It has been shown that if the cellulose hydroxyls can be made equally available for reaction by operating in solution or by allowing the reaction to come to an equilibrium, products of an acceptable and easily definable degree of uniformity can be obtained. There still remains the question of the ease of combining the requirements for availability of the cellulose with the chemical requirements necessary for a reaction to occur and for the degradation to be held within acceptable bounds. These questions will now be given a short discussion for each of the common types of reaction of cellulose. For further details of individual substitution and degradation reactions, the subsequent sections of this Chapter IX must be consulted.

(a) ESTERIFICATION

(*1*) *Direct Equilibrium Esterification with Strong Acids*

A number of strong acids will react directly with cellulose with a speed such that degradation is held within acceptable bounds. Nitric acid is the foremost example, but sulfuric acid will also work well. Formic acid is a border-line example. The outstanding characteristics of the acids that work well are that relatively concentrated solutions in water will dissolve cellulose, crystalline addition complexes with cellulose may be obtained, the equilibrium degree of esterification is high in the presence of a small amount of water, and the rate of degradation of the product in acid medium is lower than that of cellulose. Another characteristic of these acids is that their esters do not hydrolyze in a normal manner in alkali. Nitrate esters suffer profound degradation in alkaline medium, with little or no production of nitrate ion. Sulfuric half-esters (which alone are produced when sulfuric acid acts on cellulose) act like alkylating agents on alkaline hydrolysis. If at all possible, they tend to form ether linkages with other hydroxyls rather than to form free hydroxyl groups. Apparently, the cellulose oxygen holding the sulfate group may be lost on alkaline hydrolysis.

Most other strong acids do not esterify cellulose because the hydrolysis constant of the product is unfavorable. There is some evidence that anhydrous phosphoric acid esterifies cellulose slightly.[47] Perchloric acid cannot form normal esters. Halogen acids are abnormal in that the cellulosic hydroxyls are split off during reactions. These acids also degrade cellulose very rapidly. Anhydrous halogen acids are also not good swelling agents.

The tendency of nitric acid and sulfuric acid to dissolve the reaction product can be modified by the addition of other substances while still maintaining enough swelling to ensure equilibrium nitration or sulfation. The nitrate and, to a lesser extent, the sulfuric half-ester are the only well-known examples of cases where a uniform ester of intermediate substitution can be obtained by a reaction with acids with retention of fiber structure.

(2) *Organic Esters Prepared under Acidic Conditions*

As explained previously, the direct esterification of cellulose with organic acids is not a satisfactory reaction for two reasons. The equilibrium constant is unfavorable. This necessitates the use of media high in organic acid content and low in water content. Such media are very poor swelling agents for cellulose, so that the reaction is nonhomogeneous and slow. The second reason is that the rate of degradation is comparable with the rate of esterification with organic acids whether the reaction is catalyzed or uncatalyzed.

The degradation has less relative effect if the driving force for acetylation is increased above that possible in an equilibrium reaction. This is done in practice by the use of acetic anhydride. With this reagent, the equilibrium substitution product is the triacetate. It would still be possible to secure a uniform partially substituted cellulose acetate by direct reaction if a medium were available in which the reaction could be carried out in solution from the beginning. At this point, however, chemical incompatibilities become important, since there are very few anhydrous solvents for cellulose which would not destroy the acetic anhydride or react with the cellulose. Anhydrous sulfuric and phosphoric acids are obvious possibilities. Phosphoric acid solutions were tried by Heuser,[47] with fairly satisfactory results. Products of 20–25% acetyl content could be obtained by the use of equal parts of acetic acid and 100% phosphoric acid in what appeared to be a homogeneous reaction. By using acetic anhydride in place of acetic acid, any level of substitution up to the triacetate could be obtained. The products of D.S. 2.0–2.5 were incompletely soluble in acetone, however. The low solubility may have been due to the fact that these products were nearly completely substituted on the primary hydroxyl group. There is also some probability that solution of cellulose in concentrated phosphoric acid is not complete (Chapter X-A) and that therefore a nonuniform product was obtained. No one appears to have tried the homogeneous reaction of acetic anhydride with cellulose in solution in 100% sulfuric or trifluoroacetic acids, both of which are reported to be solvents for cellulose. It has been found,[48] however, that activated cellulose reacted with a mixture of 60 parts of acetic acid, 40 parts of acetic anhydride, and 2 parts of trifluoroacetic acid gave a fiber-free reaction mixture at a D.S. of 2.23. This product was also insoluble in acetone. There are some processes for the direct preparation of fibrous cellulose acetate of D.S. 2.0–2.5 that involve the use of large quantities of H_2SO_4. In this case, the initial product is a mixed acetate sulfate.

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[47] E. Heuser, W. Shockley, A. Adams, and E. A. Grunwald, *Ind. Eng. Chem.*, **40**, 1500 (1948).

The above results have been cited at length because they indicate that even if the long-sought goal of uniform direct acetylation of cellulose to a D.S. of 2.5 could be reached, the product might be unsatisfactory for commercial uses because of its low content of free primary hydroxyl groups.

The situation on the acid-catalyzed esterification of cellulose by organic acids and anhydrides may be summarized by the statement that it is almost but not quite impossible to combine the chemical requirements and the swelling requirements so that perfectly uniform reaction conditions can be obtained. The present commercial process, based on enough swelling to get rapid but not uniform reaction in the esterification cycle, followed by uniform hydrolysis to the desired D.S., appears to be the most satisfactory solution to the problem.

[48] P. W. Morgan, *Ind. Eng. Chem.*, **43**, 2575 (1951).

(3) *Reactions Requiring Media with No Active Hydrogens*

There are a variety of other reagents that will react with hydroxyl groups under suitable conditions to give esters. Among these are ketene and isocyanates. These reagents give very poor results with cellulose because they react vigorously with nearly all swelling agents and with all solvents for cellulose. The best that can be done is to use a highly activated cellulose and a tertiary amine as a catalyst and partial swelling agent, and to carry the reaction to completion. Even under such conditions ketene reacts unsatisfactorily because of its tendency to polymerize. Ketene can be used in an acetic acid acetylation, but under this condition it is first converted to acetic anhydride.

(4) *Esters Prepared under Basic Conditions*

Cellulose esters may be prepared from acid anhydrides and chlorides with basic rather than acid catalysts. (In spite of the fact that the base may be consumed in the reaction and therefore is a reagent, these reactions are definitely base-catalyzed. For example, sodium acetate is a catalyst for the reaction of acetic anhydride with an alcohol.) If the reaction is run under anhydrous conditions, with a tertiary amine as base, the reaction proceeds fairly rapidly but in a very nonuniform manner. There is also difficulty in the case of cellulose esters of sulfonic acids prepared from the acid chlorides because of the formation of quaternary salt derivatives of cellulose with the organic base and the replacement of the sulfonyl group by halogen. Again, this is a case where the swelling and the chemical requirements are incompatible.

Acid halides may also react with alkali cellulose. This is a surprisingly satisfactory reaction, not nearly as much reagent being wasted in side reactions as might be expected. The uniformity considerations are entirely analogous to those in etherification.

Some attempts have been made to prepare cellulose halides by the use of such reagents as thionyl chloride in pyridine. It has been impossible to secure uniform, soluble products, and degradation appears to be severe. This degradation appears to be a necessary consequence of any reaction which removes the hydroxyl groups from cellulose.

(b) ADDITION COMPOUNDS AND SOLUTIONS OF CELLULOSE

From the standpoint of reaction rate, the use of addition compounds of cellulose as intermediates for the preparation of their derivatives is of great interest. Those stable in the presence of water are formed very rapidly. The crystalline structure of cellulose is greatly disorganized in the addition compounds, and this disorder is partially maintained on regeneration. This use of addition compounds enables the ready activation of cellulose for other reactions. The addition complexes of cellulose with acids, bases, salts, and especially copper are also involved in all of the so-called solvents for cellulose. It is not cellulose itself that dissolves, but a compound (Chapter X-A).

Since the addition compounds are formed and decomposed very rapidly, there is little interest in the kinetics of their reactions. The equilibria involved are, however, important. There has been much confusion in this field because of the neglect of some of the principles of the phase rule and of the statistical principles of cellulose reaction. For example, attempts have been made to determine the composition of cellulose addition compounds by precipitating the addition compound from solution. The assumption is implied that the ratio of complexing reagent to cellulose is the same in the precipitate as in solution. With reactions that proceed as rapidly as the formation and decomposition of cellulose addition compounds, this assumption is entirely unjustified. The cases where this mistake has been made in the literature will not be listed. Rather, it will be pointed out that there are entirely valid methods that can be applied to the solutions themselves. The examination of the variation of optical rotation, of pH, or of light absorption as the ratio of cellulose to complexing reagent is varied is an example.[49]

Even in the case of the solid, crystalline complexes the determination of the combining ratio is not simple. The lattices of the addition compound are maintained with only slight, continuous change over a wide variation of composition of the compound. The case is thus somewhat analogous to the formation of a continuous series of mixed crystals. This question is discussed in more detail in Section D of this Chapter IX and in Chapter IV-B.

(c) CELLULOSE ETHERS

The chemistry of the formation of cellulose ethers is usually based on (1) the Williamson reaction of an alkyl halide, sulfate, or sulfonate on a derivative of cellulose with a strong base, or (2) the addition of an active reagent such as ethylene oxide, acrylonitrile, formaldehyde, or acetylene to the hydroxyl group. (The reaction of diazomethane discussed in Section E of this Chapter IX is an exception.) The technical problems are associated with the difficulty of securing uniformity of reaction and the wastage of reagents by reaction with water. There is no difficulty with degradation in any of the commercial processes, since cellulose does not degrade rapidly in aqueous alkaline media in the absence of oxygen, and the products are even more stable under these conditions.

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[49] P. Job, *Ann. chim.*, [10], 9, 113 (1928); W. C. Vosburgh and R. G. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

(1) *Aqueous Alkaline Reaction Media*

With most of the ethers, there is no possibility of securing a uniform product by either reacting to an equilibrium condition or removing substituents from a trisubstituted product. The control of uniformity depends therefore on maintaining uniform availability of the cellulose. As indicated previously, fibrous alkali cellulose gives sufficient uniformity of products for most purposes. In this case, the chief problem becomes that of side reactions leading to wastage of reagent. As the amount of water in the system is reduced, this wastage becomes in general less but the uniformity may also suffer.

All of the usual ethers may be prepared from aqueous alkaline solutions of cellulose or from solutions of cellulose esters and may therefore be secured in the uniformly substituted condition. This method is too expensive for commercial utilization. The large amount of water present and the low concentration of base both lead to excessive wastage of reagent in side reactions. As etherification media, the quaternary base solvents for cellulose are expensive and difficult to recover. The pretreatments necessary to secure solubility of cellulose in 10% NaOH are also expensive. However, there has not been enough use of homogeneous etherification for scientific purposes, in order to secure suitable materials for the determination of D.P.–viscosity relationships and the like.

(2) *Anhydrous Etherification by Use of Metal Derivatives*

Attempts to secure greater economy of reagents in etherification by the use of anhydrous metal derivatives of cellulose have failed, as is pointed out in Section E of this Chapter IX. Even when alkali cellulose is dried to the point where the residual NaOH solidifies, reaction ceases.[50] These observations indicate the importance of swelling.

A point that is frequently neglected in the consideration of anhydrous etherification conditions is the relatively rapid degradation of the anhydrous metal derivatives.

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[50] J. Chédin and A. Tribot, *Mém. services chim. état,* **33,** 169 (1947).

(3) *Equilibrium Etherification*

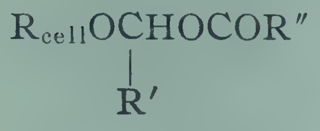
The normal alkylating agents, such as alkyl halides, cannot give equilibrium etherification to a point short of completion under alkaline conditions. This statement is made advisedly, in spite of statements to the contrary in the literature. Just as in the case of the use of acid anhydrides in esterification, the free energy change or driving force is enormous in the etherification reaction and the reaction must go to completion if given sufficient time.

The base-catalyzed addition reactions of olefins bearing activating groups, such as acrylonitrile, do not belong in the same category as alkyl halides or sulfates. The reaction of formation of cyanoethyl cellulose is reversible, and an equilibrium degree of substitution governed by the composition of the reaction medium is theoretically possible. The practical difficulty remains that consumption of reagent in side reactions and hydrolysis of cyanoethyl cellulose to carboxyethyl cellulose will proceed continuously. In order to secure an equilibrium reaction, it would be necessary to feed acrylonitrile and NaOH, while removing sodium acrylate (by crystallization, for example) until a stationary state had been established. The product would be a mixed cyanoethyl carboxyethyl cellulose. No attempt seems to have been made to realize such an equilibrium etherification in practice.

(4) *Acid-Catalyzed Etherification*

Since most chemists are aware that ethyl ether can be made from ethyl alcohol by using acid catalysts, there has been no lack of attempts to translate this type of reaction to cellulose. It was soon realized that the rate of degradation of the hemiacetal bond in cellulose under any condition of acidity was enormously greater than the rate of ether formation, so that this line of attack is hopeless. A more sophisticated approach is to try the reaction of an olefin with cellulose. Here, the driving force is greater, as in the case of esterification with anhydrides. Aside from unconfirmed patent claims, there is still no evidence that even this reaction may be made to go faster than the degradation reaction.

Like most generalizations, there is an exception to the rule that ethers of cellulose cannot be made under acid-catalyzed conditions. This exception is the reaction of aldehydes with cellulose. The cross-linking reaction of formaldehyde or glyoxal on cellulose is well known, but the intractable nature of the product has prevented thorough studies of availability and uniformity of reaction up to the present. Derivatives containing substituents of the type



$$\mathrm{R_{cell}O\underset{\underset{R'}{|}}{C}HOCOR''}$$

can be made very readily by adding an aldehyde or an aldehyde derivative to a cellulose esterification bath.[51] This easy reaction of aldehydes with cellulose is paralleled by the easy reaction of aldehydes with alcohols of low molecular weight at moderate temperatures and low acidities. Cyclic acetals of cellulose, analogous to those produced from glycerol or pentaerythritol, have not been prepared as yet.

The question of the reactivity of cellulose with urea–formaldehyde, phenol–formaldehyde, or acetone–formaldehyde resins is allied to the present subject. There is good reason to believe that these resins do form ether bonds with cellulose when reacted in the presence of cellulose fibers. The Zelan process (Section E of this Chapter IX) is another example of the use of derivatives of formaldehyde in order to secure easy reaction with cellulose.

(5) *Metal Derivatives of Cellulose*

The ready preparation of the sodium and other alkali metal derivatives of cellulose is due to the fact that ammonia and the lower primary amines are good swelling agents for cellulose and at the same time are chemically compatible with the alkali metals used in the reaction (see Section D of this Chapter IX). The nonreactivity of the alkali metal derivatives with alkylating agents when they are freed of swelling agents is another indication of the importance of swelling.

(6) *Replacement of Hydroxyl Groups*

It is possible to write reactions for the replacement of the —OH groups of cellulose by such groups as —Cl, —NH_2, —CN, —SR, and many others. Alternatively, the OH group might be oxidized to a keto or acid group. These reactions, at first sight, appear to be well founded on the basis of reactions of low molecular weight alcohols. A closer inspection shows that the conditions are not very favorable. With model compounds such as propylene glycol it is very difficult to get good yields in these reactions without a host of side reactions, many of which result directly or indirectly in decomposition of the skeleton of the basic molecule. Such side reactions as formation of a double bond in the anhydroglucose ring would result in very rapid degradation of cellulose. This point will be discussed further in Section G of this Chapter IX. From the viewpoint of reactions, the essential point seems to be that any reaction conditions which so loosen a hydroxyl group that it may be removed will also loosen neighboring bonds so that the cellulose can degrade as a probable side reaction. An example would be the introduction of an —NH_2 group by preparation of the chloride from thionyl chloride and reaction of this with ammonia. There would be two displacement reactions in this case. Probably a sulfite is formed first, and the sulfite group is then replaced by chloride ion. Finally, the chloride would be displaced by ammonia. In both of the displacement reactions, extensive side reactions leading to degradation would be expected.

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[51] T. F. Murray, Jr., and H. LeB. Gray (to Eastman Kodak Co.), U. S. Patent 1,930,145 (Oct. 10, 1933); *Chem. Abstracts*, **28**, 320 (1934).

It appears to be well established that only a few hydroxyl groups of cellulose may be displaced before degradation becomes excessive. The oxidized products may be prepared with only moderate degradation, but when once formed, they are very sensitive to alkaline degradation (see Chapter III-C-3).

(d) CATALYSIS OF CELLULOSE REACTIONS

Up to this point, it has been implied that catalysts for cellulose reactions act in the same manner as catalysts for the reactions of small molecules. This is of course true. It is at the same time true, however, that in the case of cellulose some factors become important that are normally neglected in other cases. Some of these factors will now be discussed in detail.

(*1*) *Swelling Action of Catalysts*

It may be taken as a good rule of thumb that the type of interaction of a catalyst with a reagent and a hydroxyl group that leads to more rapid reaction will also lead to partial solvation of the cellulose and an increased tendency for the cellulose to swell. In such a reaction as the acid-catalyzed acetylation of glycerol with acetic anhydride it is not difficult to secure a homogeneous reaction medium. The rate of this reaction will then be determined by the acidity, regardless of the type of acid used. In the case of cellulose, however, the amount of swelling is a complicated function of the amount of acid, the strength of the acid, and the nature of the medium. It may be preferable to use as a catalyst a large amount of a relatively weak acid rather than a small amount of a strong acid, if it is desirable to secure more uniform reaction conditions.

(2) *Water Binding by Catalysts*

In the case of nitrocellulose, the interesting situation arises that sulfuric acid, which happens to be a catalyst for the reaction, is added to reduce the activity of water and to lower the solubility of the product rather than to speed up the reaction. It is used more as a deswelling agent than a swelling agent, and as a reagent rather than as a catalyst.

(3) *Bonding of the Catalyst to Cellulose*

If the reaction of glycerol with acetic anhydride is catalyzed with sulfuric acid, it is a matter of no great moment that the sulfuric acid will react initially with the glycerol to give some sulfuric half-ester. This product is still a fairly strong acid and will be able to reach all of the reaction medium by diffusion. As the reaction proceeds, most of the sulfuric half-ester groups will be replaced with acetyl groups, and a good yield will be obtained. In the case of cellulose, two disturbing factors emerge. Most of the sulfuric acid may be bound initially in the more available portions of the fiber, leaving little available for other portions until that bound initially has been displaced by acetyl groups. A nonuniformity of catalyst distribution will therefore be superimposed on the nonuniformity of availability. This effect may explain the great differences of acetylation rate that are observed, depending on when and how the sulfuric acid is added to the reaction system. Another disagreeable result of the binding of sulfuric acid is, of course, the fact that great pains must be taken to remove the bound sulfuric acid from the product.

(4) *Degradation by Catalysts*

The degradation observed during acid-catalyzed reactions of cellulose is almost entirely due to hydrolytic scission of the 1,4-glucosidic linkages of the cellulose chain. The question naturally arises as to whether it is possible by any means to increase the ratio of the esterification rate to the degradation rate. It is well established that this ratio is definitely improved as the temperature is lowered.[26] The concentration of catalyst does not appear to be an important factor as long as the temperature can be controlled. Very rapid acetylation can be obtained by the use of a high ratio of catalyst to cellulose, without excessive degradation. In fact, it would be expected that high catalyst concentration would be preferable from the standpoint of degradation, since the increased swelling would be expected to lead to more uniform reaction. In order to use high catalyst concentration in industrial practice, it is necessary to use a relatively inactive catalyst such as zinc chloride in order to be able to control the temperature.

It might be expected that the ratio of acetylation rate to degradation rate might vary from catalyst to catalyst. With some acids, such as HCl, the chain-splitting reaction can be chemically different from other cases, since a fragment of the catalyst may be bound in the product as a glucosyl chloride end group. In such a case, the degradation reaction would be expected to have a different order and a different rate, compared to the usual hydrolytic degradation reaction which definitely involves the medium (water or acetic acid) in its chemistry. This possibility has not been explored as yet.

It is usually stated that degradation is not a problem in cellulose reactions carried out in basic media. One probable exception should be noted. In the preparation of tosyl, other sulfonyl, and sulfate esters by use of the corresponding chlorides in pyridine medium, replacement of the entering group by chlorine or quaternization with the pyridine is occurring continuously. As mentioned previously, such reactions are necessarily accompanied by degradation. It may well be that this type of degradation is not as pronounced if the reaction is carried out with alkali cellulose rather than in a pyridine medium.

4. Conclusion

The whole body of evidence supports the view that the reactions of cellulose are exactly analogous to those of compounds of low molecular weight. The proper analogs must, of course, be chosen. The question of availability for reaction is not important in much of organic chemistry, but it is encountered in such reactions as the esterification of terephthalic acid and in the corrosion of metals. A reaction of glycerol that gives a 95% yield of glycerol esters and 5% acrolein might be considered satisfactory. A cellulose reaction, on the other hand, must leave more than 99% of the cellulose chain structure unaltered before it can give a technically satisfactory product.

Investigators in the cellulose field should always pose the question to themselves: Will the proposed reaction work with methyl glucoside, cellobiose, or sucrose?

B. INORGANIC ESTERS[1]

J. Barsha

Of the various inorganic esters of cellulose which could be made, the only one that has achieved large commercial production is nitrocellulose. Consequently, a discussion of inorganic esters of cellulose must become primarily a discussion of nitrocellulose, with some mention of other esters of minor importance. In addition to the interest in nitrocellulose which stems from its wide use in industry, this inorganic ester is a versatile material for studying the chemistry of cellulose. Many advances in understanding the structure and properties of cellulose have been derived from studies of nitrocellulose.

1. Nitrocellulose[2–4]

Nitrocellulose (more correctly called cellulose nitrate since it is an ester) is the oldest cellulose derivative. Braconnot in 1832 and Pelouze in 1838 had nitrated various materials including starch, wood fiber, cotton, and paper with concentrated nitric acid. However, in 1845, Schönbein nitrated cellulose with a mixture of nitric and sulfuric acids, and he is generally credited with the discovery of nitrocellulose. The early history of nitrocellulose is associated largely with attempts to manufacture it for military explosives. It was not until about 1866, when Abel showed that the stability of nitrocellulose is improved enormously by pulping the nitrated fibers in a paper beater and then washing out the retained acid, that the manufacture of nitrocellulose was established on a sound basis.

Nitrocellulose is responsible for many changes in the industrial arts and sciences. The use of the material as a propellant was the first major break from the traditional use of black powder, which had proceeded without change for centuries. The next major step in the history of nitrocellulose was the development of celluloid. Prior to the introduction of this synthetic plastic, some molding had been done with thermoplastic natural resins such as shellac, but the art of molding and fabricating plastic compositions for practical purposes dates from the discovery of celluloid. Protective surface coatings made little progress and were all essentially oil or natural resin or oleoresinous compositions until the advent of nitrocellulose lacquer in the years following World War I. Other examples could be cited.

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[1] Editors' note: Because of the importance of cellulose xanthate, this ester is given separate treatment in Section F of this Chapter IX and Section C of Chapter X.

[2] A detailed account of the early history of nitrocellulose and a bibliography of all the literature up to 1920 are given by E. C. Worden, *Technology of Cellulose Esters*, Vol. 1, E. C. Worden, Millburn, N. J., 1921.

[3] Patent literature has been systematically compiled by O. Faust, *Celluloseverbindungen und besonders wichtige Verwendungsgebiete*, J. Springer, Berlin, 1935.

[4] The latest review of literature and patents is by K. Fabel, *Nitrocellulose; Herstellung und Eigenschaften*, Ferdinand Enke Verlag, Stuttgart, 1950.

As a pioneer in opening new fields for exploitation, nitrocellulose has in some instances met the fate of other pioneers and has been supplanted by other materials. However, the commercial history of nitrocellulose has been one of relatively constant growth although of changing markets. Currently, production is at a high level with lacquer being the most important industrial use.

The properties of a batch of nitrocellulose which have the greatest influence on its behavior in actual use are (1) its degree of nitration, and (2) its solution viscosity, which is a function of the molecular weight or degree of polymerization (D.P.) of the nitrocellulose. These two properties are therefore used industrially to characterize every batch of nitrocellulose.

The degree of nitration is most commonly designated by the nitrogen content expressed as per cent nitrogen or, less frequently, as the number of cubic centimeters of NO (at 0°C. and 760 mm. pressure) evolved from 1 g. of nitrocellulose. It is often convenient to designate the degree of nitration by the "degree of substitution" (D.S.) which is the average number of

TABLE 4

General Types of Manufactured Nitrocellulose

Nitrogen content, %	Field of application	Common solvents
10.7–11.2	Plastics, lacquers	Ethyl alcohol
11.2–11.7	Lacquers	Ether-alcohol; methanol; ethyl, butyl, and amyl acetates; acetone; methyl ethyl ketone
11.8–12.3	Lacquers, coated fabrics, cements	Ether-alcohol; methanol; ethyl, butyl, and amyl acetates; acetone; methyl ethyl ketone
12.0–13.5	Smokeless powder	Acetone

ıydroxyl groups nitrated per anhydroglucose unit. Although it is possible o prepare nitrocellulose covering the entire range of theoretical nitrogen ontent, the products normally manufactured fall in the broad range of 0–14% N as shown in Table 4.

In industrial practice, the solution viscosity of a batch of nitrocellulose s referred to simply as the viscosity of the nitrocellulose. In the standard nethod for determining nitrocellulose viscosity (see Chapter XII), the atter is expressed as the number of seconds required for a $^5/_{16}$-inch diameter teel ball to fall through 10 inches of a nitrocellulose solution (of specified oncentration and solvent composition) at 25°C. When the nitrocellulose iscosity is very low, it is usually measured in a capillary viscometer.[5] Commercial soluble nitrocelluloses are available in viscosities ranging from 0 centipoises to about 350,000 centipoises in 12.2% solution.

(a) PREPARATION OF NITROCELLULOSE

(1) *Cellulose for Nitration*

Cotton, the purest form in which cellulose occurs abundantly in nature, ıas been used in various forms for the manufacture of nitrocellulose. In he early days, the cotton was used in the form of skeins, rovings, or waste; his was later followed by the use of cotton linters, which are the short ibers cut from cottonseed at seed-processing mills (see Chapter VI-B). The advantages of linters over staple cotton in nitrocellulose manufacture nclude: (a) lower cost, (b) greater ease of handling and manipulation in he plant, and (c) less pulping required in purification of the smokeless-owder grade of nitrocellulose.

Many investigators have studied sources of cellulose other than cotton, specially in wartime when the demand for nitrocellulose for use in pro-ellants is very great. Some attention has been given to the preparation f cellulose from plants other than wood.[6–8] However, most of the effort as been directed toward the development of wood pulps[6,7,9] suitable for itration. It was realized early in this work that, in addition to chemical urity, the physical properties of the wood pulp are important in obtaining atisfactory nitration. In 1912, Tedesco[10] obtained results which led him

[5] *Nitrocellulose Handbook*, Hercules Powder Co., Wilmington, Del., 1952, 54 pp.

[6] M. G. Morin, *Mém. poudres*, **22**, 57 (1926).

[7] P. Demougin, *Mém. poudres*, **23**, 268 (1928).

[8] E. Afferni and C. Milani, *Ann. chim. applicata*, **30**, 248 (1940).

[9] W. Scharrnbeck, *Z. ges. Schiess- u. Sprengstoffw.*, **29**, 33, 67, 98, 133, 196, 230, 266 934).

[10] H. Tedesco, *Z. ges. Schiess- u. Sprengstoffw.*, **7**, 474 (1912).

to believe that nitrocellulose from wood pulp is much less stable than nitrocellulose from cotton. However, investigations at about the same time by Nitzelnadel[11] and also by Schwalbe and Schrimpff[12] showed that satisfactorily stable nitrocellulose for smokeless powder can be made from wood pulp. During World War I, large quantities of wood pulp (usually in the form of creped tissue paper) were nitrated in Germany. During the same period of scarcity of cotton, the nitrocellulose industry in the United States changed first from mill-run linters to second cut linters and later to hull fiber. The urgent need in 1918 for extending their supply of raw material led the Americans to investigate large-scale nitration of crepe paper but they encountered the following difficulties: (a) The product tended to gelatinize during nitration, (b) the quantity of acid retained after wringing was high, (c) the yield of nitrocellulose was only about 1.2 lb. per pound of wood pulp as compared with 1.5 lb. from cotton, and (d) dehydration of the nitrated pulp with alcohol was slower because of the physical nature of the product. Mixtures of equal parts of wood pulp and cotton linters were finally found to give a cellulose with physical form suitable for nitration, and the nitrocellulose produced from this mixture had satisfactory stability for the military explosives.[13]

Considerable progress has been made since the early twenties in the development of methods for putting wood pulp into suitable physical form for nitration and for manufacturing well-purified wood pulps suitable for making high-quality nitrocellulose. The developments in this field by the Brown Company have been described by Schur and Hoos.[14] They found that if purified wood pulp is shredded in the presence of about its own weight of water to a form resembling cotton linters and then redried, the shredded pulp can be nitrated by the same method that is used in the commercial nitration of linters. They also reported that customary nitrating equipment and mixed acid gave good results with purified wood pulp in the form of light-weight paper (tissue). Of greater practical interest was the finding by Schur[15] that pulpboard cut into small pieces can be satisfactorily nitrated in the usual equipment with a mixed acid rich in nitric acid. Other methods have also been proposed for putting wood pulp into suitable form for nitration.[16,17]

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[11] K. A. Nitzelnadel, *Z. ges. Schiess- u. Sprengstoffw.*, **7**, 257, 301, 339, 384, 409 (1912).

[12] C. G. Schwalbe and A. Schrimpff, *Z. angew. Chem.*, **27**, 662 (1914); A. Schrimpff, *Nitrocellulose aus Baumwolle und Holzzellstoffen*, J. F. Lehmann, Munich, 1919.

[13] R. G. Woodbridge, Jr., *Ind. Eng. Chem.*, **12**, 380 (1920).

[14] M. O. Schur and B. G. Hoos, *Ind. Eng. Chem.*, **29**, 26 (1937); this reference lists the various patents obtained by the Brown Company and also gives a good summary of other references on the preparation of wood pulp for nitration.

[15] M. O. Schur (to Brown Co.), U. S. Patent 1,914,302 (June 13, 1933).

The turning point in making the use of wood pulp practical for large-scale nitration as well as for other chemical treatment came in the mid-thirties with the invention in the United States of the Stern[18] shredder and process. The shredder produced short pieces of loosely felted wood cellulose with protruding fibers at the ends and edges. This physical form was admirably adapted for ready penetration of chemical reagents. The process developed for nitrating the wood pulp so shredded gave uniformly esterified nitrocelluloses, was economical and free from the undue difficulties encountered in nitrating various other physical forms of wood pulp, and utilized the usual nitrating mixtures and equipment required for the nitration of cotton linters.

By the beginning of World War II, the use of wood pulp for the manufacture of commercial nitrocellulose was well established. In Great Britain, small tablets cut from wood pulp sheets were nitrated;[19,20] in the United States, the Stern[18] process was in full commercial operation. Utilization of wood pulp for nitrocellulose for military propellants was, however, still in the experimental stage in the United States.[21] This situation was rapidly remedied so that most of the enormous tonnage of nitrocellulose used by the armed forces of the United States and its Allies was made from specially prepared coniferous wood pulps.[22]

The physical characteristics of the pulps have been shown to have an effect on nitratability. Coniferous wood pulps were found to be more suitable for nitration because smaller mechanical losses resulted than when deciduous wood pulps were used.[23] Acid retention by fibers of a variety of coniferous wood pulps was found by Schur and McMurtrie[24] to be higher

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[16] W. E. Sillick (to Eastman Kodak Co.), U. S. Patent 2,384,853 (Sept. 18, 1945); *Chem. Abstracts*, **40,** 207 (1946).

[17] D. J. Kridel (to Eastman Kodak Co.), U. S. Patent 2,393,783 (Jan. 29, 1946); *Chem. Abstracts*, **40,** 2305 (1946).

[18] R. L. Stern (to Hercules Powder Co.), U. S. Patent 2,028,080 (Jan. 14, 1936).

[19] N. Picton and Imperial Chemical Industries Ltd., Brit. Patent 336,235 (May 27, 1929); *Chem. Abstracts*, **25,** 1996 (1931); N. Picton (to E. I. du Pont de Nemours & Co.), U. S. Patent 1,872,181 (Aug. 16, 1932).

[20] N. Picton and N. S. Kelland, *Ind. Chemist*, **26,** 79 (1950).

[21] G. A. Richter, OSRD Report No. 71; also issued by U. S. Dept. of Commerce, Washington 25, D. C., OTS, PB Rept. 31203 (1941).

[22] Anon., *Paper Trade J.*, **117,** 14 (Oct. 7, 1943).

[23] L. Zapf, U. S. Dept. of Commerce, Washington 25, D. C., OTS, PB Rept. 4383 (1943).

[24] M. O. Schur and D. H. McMurtrie, *Paper Trade J.*, **127,** 51 (Sept. 23, 1948); **127,** 39 (Sept. 30, 1948).

in fibers with larger cross section. More complete nitration was obtained by Brissaud[25] with pulps which had received a final alkaline treatment during purification as well as with pulp fibers which are long, thick, and elastic (e.g., pulps from spruce and esparto). Mention should also be made of an entirely different raw material—that is, regenerated cellulose film (scrap cellophane)—which has been used in the manufacture of nitrocellulose for lacquers.[26,27]

Variations in the conditions under which cellulose loses or absorbs moisture can affect the final nitrogen content reached in nitration with HNO_3–H_2SO_4–H_2O, as well as the solubility and viscosity behavior of the nitrate produced. Brown and Purves[28] obtained nitrates with about 12.2% N from highly swollen cotton linters, whereas "collapsed" linters (obtained by wetting and redrying swollen linters) yielded nitrates with 0.1 to 0.6% less nitrogen. Tribot and Chédin[29] found that the addition of water or pyridine to cellulose increases the rate of nitration by HNO_3–H_2SO_4–H_2O. The maximum rate was obtained with cellulose containing about 1 mole of water or 0.2 mole of pyridine per anhydroglucose unit.

(2) *Nitration with* HNO_3–H_2SO_4–H_2O

Although nitric acid itself in both liquid and vapor form and also mixtures of nitric acid with a wide variety of other chemicals have been used experimentally to nitrate cellulose, the nitrocellulose industry still employs HNO_3–H_2SO_4–H_2O mixtures such as have been used for this purpose for a century. In other reactions of cellulose which are carried out on a large scale today, such as the preparation of viscose, cellulose acetate, and ethyl cellulose, the cellulose dissolves and its original fibrous structure is completely lost. In contrast to these, the nitration of cellulose is effected with complete retention of the original fiber structure, and the chief superficial changes that occur are an increase in the hardness of the fiber and, in the case of cotton, an untwisting of the convoluted fiber.

Since (as will be discussed later) cellulose nitration is an equilibrium reaction, the extent of nitration at equilibrium is governed primarily by the omposition of the mixed acid. The extent of nitration is affected to a esser degree by the ratio of mixed acid to cellulose, the final nitrogen conent being increased, within limits, by an increase in the ratio.[30] The effect f mixed acid composition on the extent of nitration was studied in great etail by Lunge and coworkers.[31–33] In one of their first series of experinents (Table 5) they attempted to prepare nitrocellulose with nitrogen content as close as possible to the theoretical maximum of 14.14%. Nearly ll of the products they obtained fell in the range of 13.5 to 13.8% N even hough some of their acid mixtures contained as much as 12.5% water. aximum nitrogen content was obtained with H_2SO_4:HNO_3 ratios beween 0.25:1 and 3:1. With ratios above 8:1, the product always conained some unnitrated cellulose and the fiber structure was attacked. n other experiments (Table 6) the ratio of H_2SO_4 to HNO_3 was kept nearly

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[25] L. Brissaud, *Mém. poudres*, **33**, 137 (1951).

[26] P. B. Cochran, M. V. Hitt, and L. V. Taylor (to E. I. du Pont de Nemours & Co.), U. S. Patent 1,997,766 (Apr. 16, 1935); U. S. Patent 2,150,205 (Mar. 14, 1939).

[27] L. L. Blyler (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,399,620 (May 7, 1946); *Chem. Abstracts*, **40**, 4214 (1946).

[28] R. K. Brown and C. B. Purves, *Pulp & Paper Mag. Can.*, **48**, No. 6, 100 (1947); see also A. Rosenthal and R. K. Brown, *Pulp & Paper Mag. Can.*, **51**, No. 6, 99 (1950).

[29] A. Tribot and J. Chédin, *Mém. services chim. état (Paris)*, **32**, 135 (1945).

TABLE 5

Effect of Mixed Acid Composition on Attainment of Maximum Nitration of Cellulose (Lunge and Coworkers[33])

Composition of mixed acid			Nitrogen in nitrocellulose, %
H_2SO_4, %	HNO_3, %	H_2O, %	
60.00	27.43	12.57	13.62
62.10	25.79	12.11	13.75
62.95	24.95	12.10	13.83
63.72	25.31	10.97	13.75
64.56	24.65	10.79	13.71
68.02	25.28	5.70	13.76
64.55	26.55	8.88	13.72
63.35	25.31	11.34	13.92
75.33	22.80	1.87	13.53
74.16	22.12	3.72	13.51
72.97	21.63	5.40	13.57
69.90	20.45	9.65	13.64
68.31	20.49	11.20	13.61
67.43	19.37	13.20	13.25
67.32	32.53	0.15	13.62
65.41	31.34	3.25	13.57
63.75	30.80	5.45	13.63
70.68	29.31	10.01	13.68

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[30] J. O. Small and C. A. Higgins, *Chemical Age*, **28**, 211 (1920).

[31] G. Lunge and E. Weintraub, *Z. angew. Chem.*, **12**, 441, 467 (1899).

[32] G. Lunge and J. Bebié, *Z. angew. Chem.*, **14**, 483, 507, 537, 561 (1901).

[33] G. Lunge, *J. Am. Chem. Soc.*, **23**, 527 (1901); this article is a summary of references 0 and 32 above.

constant at slightly less than one while the proportion of water was varied; it was found that the nitrogen content of the nitrocellulose decreased regularly with increase in the proportion of water in the mixed acid. Similar results were obtained by Schiemann and Kühne[34] and Demougin.[35]

TABLE 6

Effect of Water Content of Mixed Acid on the Degree of Nitration of Cellulose (Lunge and Coworkers[33])

Composition of mixed acid			Nitrogen in nitrocellulose, %	Solubility in ether-alcohol, %
H_2SO_4, %	HNO_3, %	H_2O, %		
45.31	49.07	5.62	13.65	1.50
42.61	46.01	11.38	13.21	5.40
41.03	44.45	14.52	12.76	22.00
40.66	43.85	15.49	12.58	60.00
40.14	43.25	16.61	12.31	99.14
39.45	42.73	17.82	12.05	99.84
38.95	42.15	18.90	11.59	100.02
38.43	41.31	20.26	10.93	99.82
37.20	40.30	22.50	9.76	74.22
36.72	39.78	23.50	9.31	1.15
35.87	38.83	25.30	8.40	0.61
34.41	37.17	28.42	6.50	1.73

Berl, Andress, and Escales[36] studied critically the literature on experimental nitrations with different mixed acids and found good agreement between the results of Lunge and coworkers,[31–33] Boltenstern,[37] and Demougin.[35] Since the final nitrogen content is determined by the composition of the spent acid in contact with the nitrocellulose rather than by that of the original dipping acid, Berl and coworkers calculated by the graphical methods of Demougin the composition of the spent acids from the composition of the dipping acids in cases where only the latter values were given. They then prepared a triangular coordinate diagram of the spent acid compositions in which lines were drawn connecting compositions which produced the same nitrogen content (see Fig. 6). Miles and Milbourn[38] have drawn a somewhat similar diagram in which the compositions shown are those of the dipping acids (see Fig. 7).

[34] G. Schiemann and S. Kühne, *Cellulosechemie*, **15**, 78 (1934).

[35] P. Demougin, *Mém. poudres*, **23**, 262 (1928).

[36] E. Berl, K. R. Andress, and E. Escales, *Beiträge zur Kenntnis der Mischsäure*, J. F. Lehmann, Munich, 1937, p. 32.

[37] W. von Boltenstern, Dissertation, Darmstadt, 1921, p. 86.

[38] F. D. Miles and M. Milbourn, *J. Phys. Chem.*, **34**, 2598 (1930).

Despite the wide variety of HNO_3–H_2SO_4–H_2O compositions (shown in Fig. 6) which can yield nitrocellulose of a given nitrogen content, the selection for industrial nitrations is fairly limited by considerations of cost and because many of the compositions exert a marked swelling or dissolving action on the fibers. In actual practice[30] (see Table 7) the different mixed acids used to produce the usual range of nitrocelluloses, with from about 10 to 13.5% N, do not vary widely in composition from each other or from the H_2SO_4:HNO_3 ratio of 3:1 originally used by Schönbein a century ago.

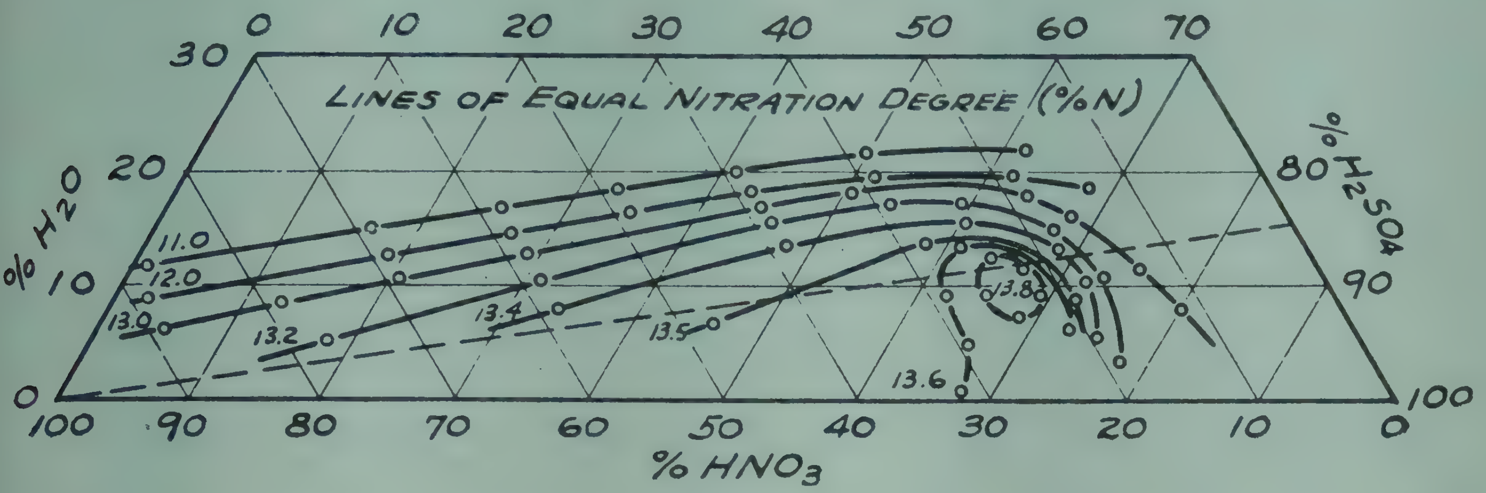

Fig. 6. Effect of spent acid composition on the nitrogen content of nitrocellulose (Berl, Andress, and Escales[36]).

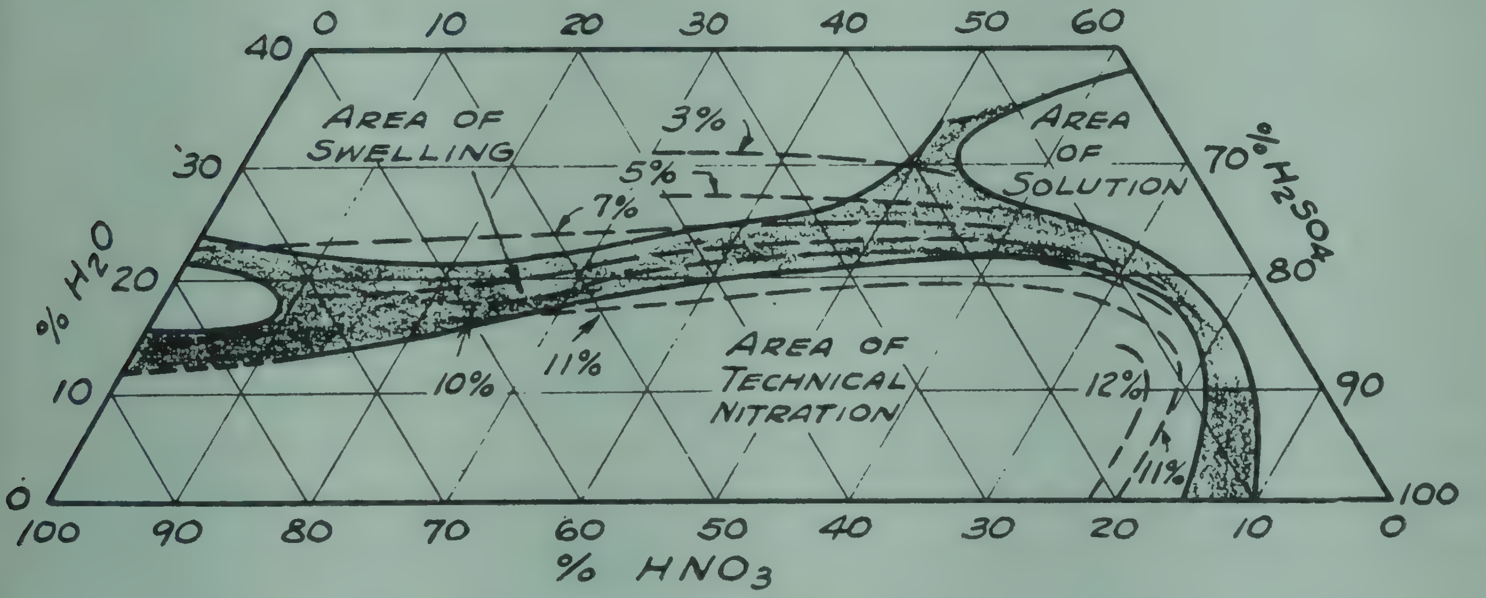

Fig. 7. Effect of dipping acid composition on the nitrogen content of nitrocellulose (Miles and Milbourn[38]).

Various investigators have recommended mixed acid compositions for the preparation of specific types of nitrocellulose.[4] Thus, Baker, Morgan, and Quaid[39] reported that nitrocellulose with 11.85–12.00% N and which is completely soluble in methanol is obtained by nitrating chemical cotton for 20 min. at 45°C. with 50 parts of mixed acid containing 27 to 32% HNO_3. With a mixed acid containing 30.7% HNO_3, 51.7% H_2SO_4, and 17.6% H_2O, they obtained nitrocellulose with 11.98% N.

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[39] L. S. Baker, I. H. Morgan, and R. J. Quaid (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,105,627 (Jan. 18, 1938).

TABLE 7

Composition of Commercial Nitrating Acids and the Nitrogen Content of Nitrocelluloses Produced by Them (Small and Higgins[30])

Nitrogen, %	HNO_3, %	H_2SO_4, %	$HNOSO_4$, %	H_2O, %
10.52	22.30	51.97	5.25	20.48
10.74	22.08	52.50	5.10	20.32
10.86	21.60	53.13	4.80	20.47
10.96	22.13	51.99	5.60	20.28
11.05	23.86	51.24	5.17	19.73
11.10	22.74	52.04	5.57	19.65
11.14	24.81	53.60	1.37	20.22
11.19	23.80	50.40	6.55	19.25
11.91	20.18	55.93	6.00	17.89
11.92	20.15	55.80	6.20	17.85
11.96	20.30	56.13	5.80	17.77
11.98	19.98	55.95	6.25	17.82
12.06	20.50	55.45	6.40	17.65
12.75	19.54	60.92	4.57	14.97
13.00	20.00	59.64	5.30	14.16
13.30	24.37	59.54	4.86	11.23

Sillick[40] reported that nitrocellulose with improved adhesion is obtained by nitrating oxidized cellulose containing 0.05 to 6% carboxyl groups in the primary position of the anhydroglucose units. He nitrated the oxidized cellulose with mixed acid containing 80 to 98% acid (40 to 60% HNO_3 and 40 to 60% H_2SO_4) and treated the product with a mild alkaline solution (e.g., NaOH, calcium acetate, or calcium hydroxide) to impart insolubility in acetone.

The nature of the cellulosic material being nitrated also plays a part in determining the composition of mixed acid to be used. Thus, Schrimpff[12] found that mixed acid must contain more nitric acid in order to nitrate wood pulp to the same extent as cotton.

The rate of cellulose nitration increases with rise in temperature (see Table 8), but the drawback to much higher nitration temperatures than are normally employed (20 to 40°C.) is excessive degradation with resultant

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[40] W. E. Sillick (to Eastman Kodak Co.), U. S. Patent 2,544,902 (Mar. 13, 1951); *Chem. Abstracts*, **45**, 4927 (1951).

TABLE 8

Effect of Temperature and Reaction Time on the Nitration of Cellulose (Lunge and Coworkers[33])

Temp., °C.	Time, hr.	Nitrogen, %	Yield, %	Yield (calculated), %
0	0.5	10.71	152.3	153
0	7	13.19	173.3	174
10	7	13.37	175.8	176
15	7	13.38	175.6	176
19	0.5	12.72	166.1	170
19	7	13.39	175.6	176
40	0.5	13.07	172.3	173
40	7	13.06	169.6	173
60	0.5	13.08	169.2	173
60	4.5	13.07	162.1	173
80	0.25	13.07	161.2	173
80	0.5	13.12	125.2	173
80	3	13.12	81.5	173

Notes: Nitration was effected with a 3:1 mixture of H_2SO_4:HNO_3.

Yields are based on the weight of cellulose employed; that is, the % yield is the weight of nitrocellulose obtained from 100 parts of cellulose.

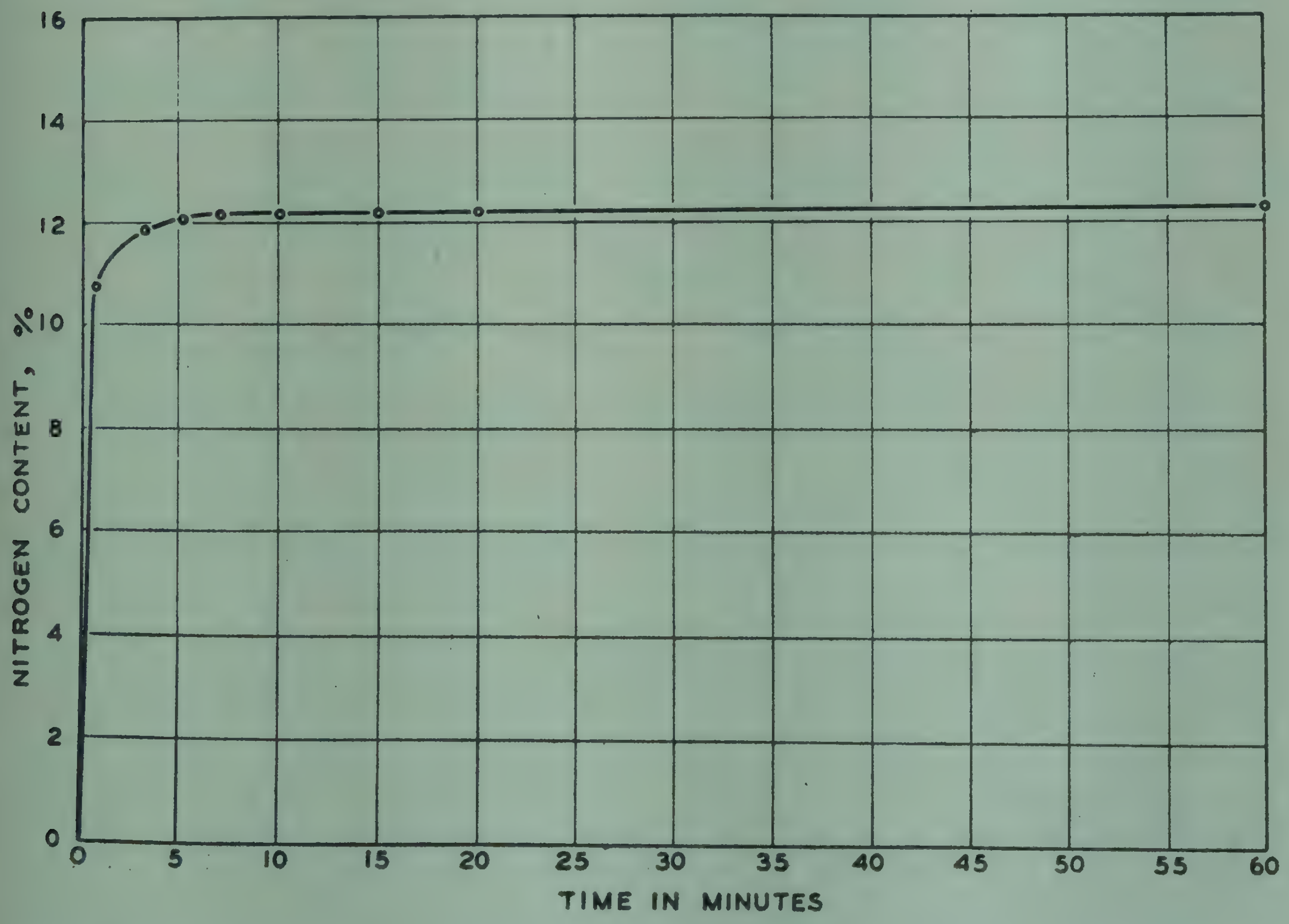

Fig. 8. Rate of nitration of cellulose in a laboratory dipping pot with mixed acid containing 21.0% HNO_3, 61.5% H_2SO_4, and 17.5% H_2O (Spalding[41]).

drop in viscosity and yield.[30,33] The nitration rate decreases markedly with increase in the $H_2SO_4:HNO_3$ ratio.[33] The nitration of cellulose takes place much more rapidly than the other cellulose reactions which are practiced industrially;[34] for most commercial types, nitration is effected in about 30 min. The extreme rapidity of cellulose nitration,[41] particularly in the first few minutes, is shown well in Figure 8.

(3) Nitration with Other Reagents

Considerable attention has been given to the use of nitration reagents other than HNO_3–H_2SO_4–H_2O, but none of them have attained industrial importance. The simplest of these reagents is aqueous nitric acid. The following data obtained by Vieille[42] indicate the extent of nitration that can be obtained with various concentrations of nitric acid:

% HNO_3	77.3	80.8	83.5	87.0	89.6	92.1	95.1
% N in nitrocellulose	6.85	8.07	8.78	10.33	11.53	12.23	12.68

Practically no nitration occurred with 75% HNO_3. In the approximate range of 80 to 85% HNO_3, the fibers dissolved completely and the nitrocellulose could be precipitated by adding water; other concentrations of HNO_3 swelled and gelatinized the fibers.

Bouchonnet and coworkers[43] nitrated cellulose with pure HNO_3 and reported that the acid in the interior of the fibers is diluted by water formed in the reaction, which, together with the heat liberated, causes gelatinization or solution of some of the nitrocellulose. This partial or complete destruction of the fibers is a major drawback to the use of HNO_3 as the sole reagent in the industrial nitration of cellulose. The addition of dehydrating salts to pure HNO_3 prevents the hardening and contraction of fibers which occur when HNO_3 is used alone. A maximum nitrogen content of 13.87% was obtained when 15 to 20% of NH_4NO_3 or 30% of KNO_3 was added to pure HNO_3 as compared with 13.3% when HNO_3 was used alone. K_2SO_4, KH_2PO_4, and $NH_4H_2PO_4$ showed a similar action. The use of 97% HNO_3 was less satisfactory than pure HNO_3.

Chédin and Tribot[44] reported results similar to those obtained by

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[41] E. B. Spaulding, Hercules Powder Co., Parlin, N. J., private communication.

[42] P. Vieille, *Mém. poudres*, **2**, 212 (1884–9).

[43] A. Bouchonnet, F. Trombe, and G. Petitpas, *Compt. rend.*, **197**, 332 (1933); *Mém. poudres*, **28**, 277 (1938); *Bull. soc. chim.*, [5], **4**, 894 (1937); see also T. Urbanski and W. Szypowski, *Roczniki Chem.*, **19**, 387 (1939); *Chem. Abstracts*, **34**, 4566 (1940).

[44] J. Chédin and A. Tribot, *Mém. services chim. état* (*Paris*), **34**, 277 (1948).

Bouchonnet and coworkers. In addition, Chédin and Tribot found that nitrocellulose with 13.2% N, obtained in one nitration with 100% HNO_3, could be made amenable to further nitration with 100% HNO_3 by dissolving the gelatinized fibers in acetone and precipitating with water. They obtained nitrocellulose with 13.7 to 13.8% N by repeated reprecipitation and treatment with 100% HNO_3.

Attempts have been made to simplify the nitration of cellulose and to overcome the disadvantages in the use of nitric acid solutions by nitrating cellulose with HNO_3 vapor.[45] Rogovin and Tikhonov[46] suspended cotton over 96% HNO_3 in a closed flask. After 4 hrs. at 20°C., the nitrogen content was only 4.96%, after 24 hrs. 11.96%, and after 96 hrs. 13.4%. Raising the temperature markedly accelerated the nitration. At 35°C., 11.05% N was attained in 4 hrs., 12.88% N in 24 hrs., and 13.44% N in 48 hrs. The nitration of cellulose with HNO_3 vapors at reduced pressures was studied extensively by a group of French investigators.[47–52] They designed special equipment to prevent condensation of HNO_3 and water vapor in the fibers.[47,48] In one series of small-scale nitrations (4 g. of cellulose) with 100% HNO_3 at 84 mm. pressure, 11.12% N was attained in 15 min. and 13.59% N in 75 min. In larger-scale nitrations[51,52] (100 g. cellulose), it was found that the mass of cellulose was not uniformly nitrated, the nitrogen content decreasing with increasing distance from the point of entry of the HNO_3 vapors. Fairly uniform products of high nitrogen content (about 13.7% N) were obtained on prolonged nitration. The preparation of uniform nitrocellulose corresponding to industrial types (10.7 to 12.3% N) was not demonstrated. In a study of the kinetics of the nitration of ramie cellulose with HNO_3 vapors, Wilson and Miles[53] showed by means of fractionation and solubility tests that homogeneous products were not obtained by this process.

Nitrogen oxides have been used experimentally to nitrate cellulose. Products with 11.30 to 11.95% N were obtained on nitrating cellulose with liquid NO_2 at 10°C. for 48 hrs.[54] Pinck[55] found that nitrocellulose of any desired nitrogen content could be prepared with a nitrating bath in which HNO_3 had been replaced by N_2O_4. An increase in the amount of N_2O_4 in the usual nitration mixture (HNO_3–H_2SO_4–H_2O) decreases the yield[56] and nitrogen content[56,57] of the nitrocellulose. The degree of nitration with N_2O_4–HNO_3 mixtures reaches a maximum at 30% N_2O_4.[58] Addition of nitrogen oxides to nitric acid (in absence of sulfuric acid) causes a higher degree of nitration (a maximum with N_2O_5); N_2O_3 and N_2O_4 cause greater depolymerization of cellulose than N_2O_5. Addition of 5% N_2O_5 to 95% HNO_3 yields nitrocellulose with 13.7% N compared to 13.0% N with 96% HNO_3 alone. The more vigorous action of N_2O_5 in comparison with P_2O_5 can be explained by the more rapid diffusion into the interior of the fiber and greater esterification in the interior by the HNO_3 resulting from the combination of N_2O_5 with water.[59] Dalmon and coworkers[60] treated cellulose with N_2O_5 dissolved in carbon tetrachloride at 130°C. for 6 hrs. in the dark and obtained a high yield of nitrocellulose with about 14% N. Similar results were obtained by Caesar.[61] Treatment of dry cotton with pure N_2O_5 in a current of dry air or oxygen yielded pure cellulose trinitrate with 14.12% N.[62] X-ray diagrams taken at frequent intervals during nitration with N_2O_5 vapor showed that the structure progressed through all the stages between cellulose and cellulose trinitrate.[63]

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[45] Deutsche Celluloidfabrik, German Patent 269,246 (Jan. 16, 1914); *Chem. Abstracts,* **8,** 2060 (1914).

[46] Z. A. Rogovin and K. Tikhonov, *Cellulosechemie,* **15,** 102 (1934).

[47] A. Bouchonnet and F. Trombe, *Bull. soc. chim.,* [5], **5,** 715 (1938).

[48] F. Trombe, *Bull. soc. chim.,* [5], **9,** 526 (1942).

[49] A. Bouchonnet, F. Trombe, and G. Petitpas, *Mém. poudres,* **28,** 308 (1938).

[50] G. Champetier and M. Foëx, *Compt. rend.,* **211,** 468 (1940); *Bull. soc. chim.,* [5 **8,** 115 (1941); *Bull. soc. chim.,* [5], **9,** 711 (1942).

[51] M. Foëx, *Bull. soc. chim.,* [5], **8,** 381, 390 (1941).

[52] F. Trombe, M. Foëx, and G. Champetier, *Ann. chim.,* [12], **4,** 745 (1949).

[53] G. L. Wilson and F. D. Miles, *Trans. Faraday Soc.,* **40,** 150 (1944).

The replacement of sulfuric acid by phosphoric acid in nitrating acid has interested many investigators because nitrocelluloses of high stability are readily obtained. Krauz and Blechta[64] nitrated cellulose for 1 hr. at 20°C. with a mixed acid containing 50% H_3PO_4, 48.2% HNO_3, and 0.34% water and obtained nitrocellulose with 12.93% N. When they increased the water content of the mixed acid they observed a rapid drop in nitrogen content and a sharp increase in the dissolving action of the nitrating acid on the nitrocellulose. With essentially anhydrous HNO_3–H_3PO_4 mixtures, they found that the nitrogen content dropped from 12.93% N with a 1:1 ratio of HNO_3:H_3PO_4 to 11.36% N with a 1:8 ratio of HNO_3:H_3PO_4.

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[54] C. J. Staud and J. T. Fuess (to Eastman Kodak Co.), U. S. Patent 1,917,400 (July 11, 1933).

[55] L. A. Pinck, *Ind. Eng. Chem.*, **22**, 1241 (1930); U. S. Patent 1,784,945 (Dec. 16, (1930).

[56] S. S. Mindlin and L. I. Kuz'mina, *J. Applied Chem.* (*U. S. S. R.*), **8**, 1415 (1935).

[57] L. Brissaud, *Mém. poudres*, **30**, 217 (1948).

[58] P. P. Shorygin and E. V. Khait, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 188 (1937).

[59] Z. A. Rogovin and K. Tikhonov, *Cellulosechemie*, **16**, 11 (1935).

[60] R. Dalmon, J. Chédin, and L. Brissaud, *Compt. rend.*, **201**, 664 (1935).

[61] G. V. Caesar (to Stein, Hall & Co., Inc.), U. S. Patent 2,400,287 (May 14, 1946); *Chem. Abstracts*, **40**, 4487 (1946); U. S. Patent 2,432,280 (Dec. 9, 1947).

[62] R. Dalmon, *Compt. rend.*, **201**, 1123 (1935); see also T. Urbanski and Z. Janiszewski, *Roczniki Chem.*, **17**, 349 (1937).

[63] M. Mathieu, *Compt. rend.*, **212**, 80 (1941).

[64] C. K. Krauz and F. J. Blechta, *Chem. News*, **134**, 1, 17 (1927).

Berl and Rueff[65] nitrated dry cellulose for 4 hrs. at 19°C. with H_3PO_4–HNO_3 (1:1) containing a little P_2O_5 and obtained a product with 14% N. The nitrocelluloses they prepared with H_3PO_4–HNO_3 mixtures (anhydrous or containing some P_2O_5) had much higher viscosity and nitrogen content than those obtained with HNO_3–H_2SO_4 mixtures. Under certain conditions, nitration with HNO_3–H_3PO_4–P_2O_5 was very rapid and a nitrocellulose with 13.5% N was obtained in 1.5 min.[66] In experiments aimed at obtaining maximum nitration, Lenze and Rubens[67] obtained nitrocellulose with 14% N by nitrating with HNO_3–P_2O_5 mixtures; the optimum proportion of P_2O_5 was 2.5%. Davidson[68] carried out numerous nitrations with a mixture of 48% HNO_3, 50% H_3PO_4, and 2% P_2O_5 for 4 hrs. at 0°C.; the nitrocelluloses contained 13.7% N and about 0.3% P.

The ability of HNO_3–H_3PO_4–P_2O_5 mixtures to yield nitrocelluloses with little or no degradation[68–70] has resulted in their use in scientific work for the conversion of cellulose samples to a form which is soluble in organic solvents and which can therefore be used in the determination of molecular weights and molecular weight distribution.

Bouchonnet and coworkers[71] investigated a wide range of nitrating acid compositions based on phosphoric acid with the object of determining their usefulness for industrial nitration. They concluded that H_3PO_4–HNO_3 mixtures could be used for the preparation of nitrocelluloses[72] with 11.7–12.2% N and 12.9–13.4% N. Products with satisfactory stability were obtained after only a boiling water treatment. A comprehensive study of the same subject carried out at Poudrerie Nationale d'Angoulême[73] in France led to a somewhat different conclusion. In their opinion, H_3PO_4–

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[65] E. Berl and G. Rueff, *Ber.*, **63B**, 3212 (1930); *Cellulosechemie*, **12**, 53 (1931); see also E. Berl, U. S. Patent 2,384,415 (Sept. 4, 1945); *Chem. Abstracts*, **40**, 206 (1946).

[66] E. Berl and G. Rueff, *Cellulosechemie*, **14**, 109 (1933).

[67] F. Lenze and E. Rubens, *Z. ges. Schiess- u. Sprengstoffw.*, **26**, 4 (1931); **27**, 114, 154 (1932).

[68] G. F. Davidson, *J. Textile Inst.*, **29**, T195 (1938).

[69] E. Berl and G. Rueff, *Cellulosechemie*, **14**, 115 (1933).

[70] H. Staudinger and R. Mohr, *Ber.*, **70B**, 2296 (1937).

[71] A. Bouchonnet, F. Trombe, and G. Petitpas, *Bull. soc. chim.*, [5], **4**, 560 (1937).

[72] The common French designations for these nitrocelluloses are: CP_2 guncotton for 11.7–12.2% N content and CP_1 guncotton for 12.9–13.4% N content.

[73] Poudrerie Nationale d'Angoulême, *Mém. poudres*, **28**, 82 (1938).

HNO_3 mixtures are not suitable for producing nitrocelluloses with about 12% N because the composition of the nitrating mixture must be kept very close to 20% HNO_3, 56% P_2O_5, and 24% H_2O. Any slight deviations from this composition yield mixtures which crystallize or which harden the nitrocellulose fibers. Greater latitude is possible with the acid mixtures producing nitrocelluloses with about 13% N. In the case of both 12 and 13% N nitrocellulose, slight deviations in the water content of the nitrating acids produce significant variations in nitrogen content. This would cause difficulty in controlling the degree of nitration in industrial nitration. The best use for H_3PO_4–HNO_3 mixtures seems to be in the production of nitrocelluloses with high nitrogen content. Thus H_3PO_4–HNO_3 compositions melting at 0°C. are available which yield nitrocellulose with 13.75% N; these compositions do not attack the fiber structure and should therefore permit the ready separation of the nitrocellulose from the spent acid.

Nitration with the conventional nitric–sulfuric mixed acids containing organic diluents has also been investigated. A mixed acid emulsion containing CCl_4 or pentane and stabilized with a few drops of naphthalenesulfonic acid yielded products with about 11% N and fairly good solubility; the acid mixture contained much less HNO_3 and H_2SO_4 than usual.[74] Brissaud[75] reported that the CCl_4–mixed acid emulsion breaks on contact with the fibers and that the mixed acid is absorbed by the fibers. The mixed acid retention after centrifuging is the same as in normal nitration and no economy in acid consumption is obtained. To avoid the gelation of fibers which occurs on nitrating cellulose with concentrated HNO_3 alone, Trogus[76] used a mixture of HNO_3 and glacial acetic acid. To obtain nitrocelluloses with over 12.5% N, it was advantageous to have present a small amount of water-binding agent such as acetic anhydride or P_2O_5. Watanabe[77] found that cellulose was nitrated rapidly by mixtures of CCl_4 and HNO_3; with mixtures containing CCl_4, HNO_3, and acetic anhydride, the maximum nitrogen content of over 13% was obtained only when the HNO_3 concentration was 45 to 50%. Darzens[78] nitrated cellulose with a homogeneous mixture of HNO_3–acetic anhydride–chloroform and obtained a product with 13.7% N. Further study of this process showed that nitration is effected very slowly and that the products are insoluble in ether–alcohol.[79]

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[74] Z. A. Rogovin and P. Paradnya, *Cellulosechemie*, **15**, 32 (1934).

[75] L. Brissaud, *Mém. poudres*, **30**, 205 (1948).

[76] C. Trogus, *Ber.*, **64B**, 405 (1931); see also G. Petitpas, *Mém. services chim. état (Paris)*, **30**, 248 (1943).

[77] S. Watanabe, *J. Soc. Chem. Ind., Japan*, **45**, 829, 832 (1942); *Chem. Abstracts*, **43**, 1967 (1949).

[78] G. Darzens, *Mém. poudres*, **25**, 437 (1932–3).

In experiments aimed at obtaining maximum nitration, nitrocelluloses with about 14% N were obtained by nitration with mixtures containing pure HNO_3 and acetic, propionic, or butyric acid. Nitration with a mixture containing 50% HNO_3, 25% acetic acid, and 25% acetic anhydride for 5 hrs. at 15°C. yielded nitrocellulose with 14.08% N. By extraction of this product with boiling ethyl alcohol, cellulose trinitrate (14.14% N) with good stability was obtained.[80] Chédin[81] and Tribot[82] studied the nitration of cellulose with a variety of HNO_3–acetic anhydride mixtures and with acetyl nitrate, which is a strong nitrating agent. They found that dry cellulose fibers were nitrated to only a slight extent (about 1% N) by acetyl nitrate and by HNO_3–acetic anhydride mixtures containing less than 20% HNO_3 in which an appreciable amount of acetyl nitrate is formed. A high degree of nitration (up to 13.7% N) was obtained when the cellulose fibers were first activated by steeping them successively in water, glacial acetic acid, and acetic anhydride. Petitpas and coworkers[83,84] nitrated cellulose with mixtures containing HNO_3 and a diluent (ether, β-dichloroethyl ether, acetic acid, propionic acid, acetic anhydride, chloroform, or phosphoric acid) with the object of determining the effect on nitration of the basicity of the oxygen in the diluent. No nitration occurred with ether as the diluent. With the other diluents, nitration was progressively increased as the basicity of the oxygen in the diluent decreased.

It should be pointed out that the use of mixtures of HNO_3 and acetic anhydride can be very dangerous because of the formation of acetyl nitrate which explodes at elevated temperatures.

The nitration of cellulose with HNO_3–methyl nitrate mixtures under a wide variety of conditions was studied by Rogovin and coworkers.[85] Nitration for 2 hrs. at 35°C. with a 2:3 ratio of HNO_3 (100%) to methyl nitrate yielded nitrocellulose with 13.7 to 14.0% N; nitration with 95% HNO_3 under the same conditions resulted in 10.1% N. Most of the nitrocelluloses with over 10% N dissolved completely in the nitrating mixture and were precipitated by pouring into water. Replacement of up to 60% of the methyl nitrate by methylene chloride or ethylene dichloride resulted in nitrocelluloses with over 10% N and with improved solubility.

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[79] L. Brissaud, *Mém. poudres*, **25**, 440 (1932–3).

[80] A. Bouchonnet, F. Trombe, and G. Petitpas, *Compt. rend.*, **197**, 63 (1933); *Bull. soc. chim.*, [5], **4**, 1085 (1937); *Mém. poudres*, **28**, 295 (1938).

[81] J. Chédin, *Kolloid-Z.*, **125**, 65 (1952).

[82] J. Chédin and A. Tribot, *Bull. assoc. tech. ind. papetière*, **5**, 435 (1951); *Mém. services chim. état* (*Paris*), **36**, 31 (1951).

[83] J. Desmaroux, R. Dalmon, and G. Petitpas, *Compt. rend.*, **212**, 396 (1941).

[84] G. Petitpas, *Mém. services chim. état* (*Paris*), **30**, 243 (1943).

[85] Z. A. Rogovin, K. Tikhonov, and A. Maslova, *J. Applied Chem.* (*U. S. S. R.*), **19**, 659 (1946); *Chem. Abstracts*, **41**, 6044 (1947).

(4) *Mechanism of Nitration*

According to evidence presented by Berl and coworkers[86] and other investigators,[87,88] cellulose nitration involves the usual principle of esterification; that is, when molecular quantities of an acid and an alcohol react, an ester is formed and water is split out. Since the reverse reaction also takes place at the same time, an equilibrium will be set up among acid, alcohol, water, and ester. The reaction is forced to completion by displacement of the equilibrium when an excess of one component (in this case the HNO_3) is used, and H_2SO_4 is added to combine with the water formed. This equilibrium between the nitrocellulose and the nitrating medium has been found to occur over a wide range of substitution, the nitrogen content of the nitrocellulose being determined by the final composition of the nitrating bath rather than by the composition of the original mixed acid. The evidence of the existence of this equilibrium includes the observation that the equilibrium can also be approached from the other direction; that is, long contact of nitrocellulose with relatively dilute mixed acid causes partial denitration and production of a nitrocellulose with the same nitrogen content as would be obtained by direct action of this mixed acid on cellulose. Kagawa[89] has claimed that the reaction temperature has no effect on the nitrogen content attained at equilibrium.

Various investigators have attempted to determine the properties of mixed acids which influence their nitrating capacity. Sapozhnikov[90] determined the nitric acid vapor pressure of various mixed acids and the nitrogen content of the nitrocelluloses produced by them. He observed a close relation between these values and found that the highest nitrogen content was attained with the mixed acid having the highest HNO_3 vapor pressure. Berl and coworkers[36] confirmed and extended the work of

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[86] E. Berl and R. Klaye, *Z. ges. Schiess- u. Sprengstoffw.*, **2**, 403 (1907); E. Berl and E. Berkenfeld, *Z. angew. Chem.*, **41**, 130 (1928); E. Berl and O. Hefter, *Cellulosechemie*, **14**, 65 (1933).

[87] P. Demougin and Bonnet, *Mém. poudres*, **24**, 147 (1931).

[88] K. Fabel and H. Fritzsche, *Nitrocellulose*, **10**, 3, 24 (1939).

[89] I. Kagawa, *J. Soc. Chem. Ind., Japan*, **44**, Suppl. binding, 130 (1941).

[90] A. Sapozhnikov, *Z. ges. Schiess- u. Sprengstoffw.*, **1**, 453 (1906); **4**, 441, 462 (1909); see also C. Kullgren, *Z. ges. Schiess- u. Sprengstoffw.*, **3**, 146 (1908).

Sapozhnikov. They pointed out that, according to their triangular diagram (Fig. 6) in which the points corresponding to HNO_3 vapor-pressure maxima are joined by the broken line, there is an increase in nitrogen content with decrease in water content on approaching the broken line and that the maximum nitration is attained with a spent acid whose composition lies on this line.

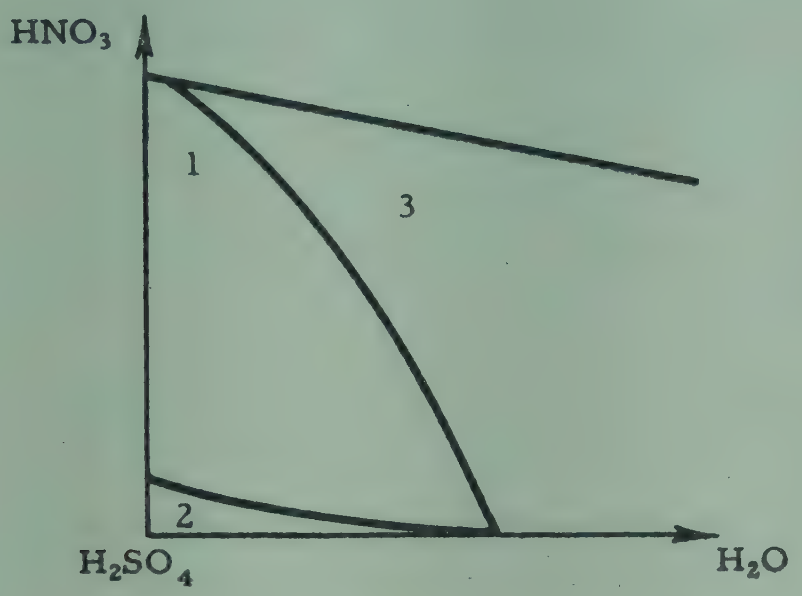

Fig. 9. Composition of mixed acids and esterification effectiveness (Chédin[91b]). Zone 1, nitrocellulose obtained approaches trinitrate; zone 2, no nitration; the cellulose undergoes degradation; zone 3, degree of nitration at equilibrium varies inversely with degree of hydration of HNO_3.

Chédin and coworkers[91–95] carried out an extensive investigation of the composition of HNO_3–H_2SO_4–H_2O mixtures by means of Raman spectrography. On the basis of their results, they divided the ternary diagram of mixed acid compositions into three zones as shown in Figure 9. In Zone 2, in which the mixed acids are made up with high concentrations of H_2SO_4 and low concentrations of HNO_3 and H_2O, all of the HNO_3 is present in the form of nitronium ions (NO_2^+). Mixed acids in this zone cause considerable degradation of the cellulose and effect little or no nitration. In Zone 1, the original mixed acids are richer in nitric acid; all the nitric acid is present in the form of HNO_3 and NO_2^+ ions with none being hydrated, and the H_2SO_4 is more or less hydrated. All of the mixed acids in Zone 1

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[91] J. Chédin, *Mém. services chim. état (Paris)*, (*a*) **31,** 154 (1944); (*b*) **32,** 108 (1945).

[92] J. Chédin, S. Fénéant, and G. Watelle, *Mém. services chim. état (Paris)*, **33,** 127 (1947); *Compt. rend.*, **224,** 1008 (1947).

[93] J. Chédin and A. Tribot, *Mém. services chim. état (Paris)*, **33,** 143 (1947).

[94] J. Chédin, A. Tribot, and S. Fénéant, *Compt. rend.*, **226,** 2068 (1948).

[95] J. Chédin, *Chimie & industrie*, **61,** 571 (1949); this paper reviews the work covered in references 91 to 94.

yield nitrocelluloses with the same high nitrogen content (about 13.75%) approaching that of cellulose trinitrate. The failure to attain the theoretical nitrogen content of 14.14% N (that is, the completely trisubstituted product) with HNO_3–H_2SO_4–H_2O mixtures can be best explained by the ability of H_2SO_4 to enter into the esterification reaction in competition with HNO_3 and the resultant formation of sulfuric–nitric mixed esters.[96] In Zone 3, nitronium ions could not be detected spectrographically. Chédin and coworkers determined by spectrographic and calorimetric examination of the mixed acid in Zone 3 that the water is partitioned between HNO_3 and H_2SO_4. They also determined that the degree of nitration attained at equilibrium by mixed acids in Zone 3 decreases with increasing degree of hydration of HNO_3. Mixed acids with different compositions but with the same degree of hydration of HNO_3 yield nitrocelluloses with equal nitrogen contents.

The formation of intermediate compounds during the nitration of cellulose has been studied by various investigators. Katz, Hess, and Trogus[97–99] found that the $[C_6H_{10}O_5 \cdot HNO_3]_x$ addition compound reported by Knecht[100] has a constant composition (as indicated by the formula) and a characteristic x-ray diagram; on washing with water, this addition compound yields a regenerated cellulose with the x-ray diagram of mercerized cellulose. Miles[101] found that the x-ray diagram of fibers obtained by denitrating nitrocelluloses of Classes I and II (so designated by Miles and Craik[102]) shows them to consist almost entirely of mercerized cellulose. It is therefore probable that some constituent of the nitrating mixture must have penetrated the whole structure. The results of Katz and Hess[97] suggest that it is the HNO_3 that must penetrate the micelle. Carrière[103] found a higher $HNO_3 : H_2SO_4$ ratio in the water in which nitrocellulose is drowned after nitration than in the wringer acid and suggested that a "pernitrocellulose," having more than the theoretical nitrogen content for cellulose trinitrate, is formed during nitration and decomposed on contact with water. Demougin and Bonnet[104] studied this phenomenon and obtained results which indicate that the excess HNO_3 is selectively adsorbed by the nitrocellulose, and is not present as a chemical compound. Berl and Rueff[105] treated nitrocellulose with pure HNO_3 or mixed acids and obtained an adsorption product (14.8% N) similar to that of Knecht[100]; water decomposed it to nitrocellulose and HNO_3. X-ray diagrams, after treatment of cellulose with dry HNO_3, showed spots due to cellulose, nitrocellulose, and Knecht's compound.

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[96] K. A. Hofmann, *Sitzber. preuss. Akad. Wiss., Physik.-math. Klasse*, **1933**, 800.

[97] J. R. Katz and K. Hess, *Z. physik. Chem.*, **122**, 126 (1926).

[98] C. Trogus, *Cellulosechemie*, **15**, 104 (1934).

[99] C. Trogus and K. Hess, *Z. Elektrochem.*, **40**, 193 (1934).

[100] E. Knecht, *Ber.*, **37**, 549 (1904).

[101] F. D. Miles, *Trans. Faraday Soc.*, **29**, 110 (1933).

[102] F. D. Miles and J. Craik, *Nature*, **123**, 82 (1929); *J. Phys. Chem.*, **34**, 2607 (1930).

[103] E. Carrière, *Bull. soc. chim.*, [4], **39**, 438 (1926).

[104] P. Demougin and Bonnet, *Mém. poudres*, **24**, 157 (1931).

Various investigators have sought to determine the effective nitrating agent in nitrations with HNO_3–H_2SO_4–H_2O mixtures. Farmer[106] proposed that esterification of cellulose with HNO_3 proceeds through its "pseudo" form ($O_2N \cdot OH$). Other investigators[107–110] have obtained evidence which shows that the NO_2^+ ion is the effective nitrating agent in the nitration of aromatic molecules with mixed acids. By analogy, it has been suggested that in the nitration of starch there is an electrophilic attack on the hydroxyl oxygen by the NO_2 ion followed by elimination of a proton.[111] A similar hypothesis for the mechanism of nitration of cellulose is supported by the observation that nitration of ordinary cellulose with O^{18}-enriched mixed acid yields nitrocellulose with nitrate groups in which only two of the three nitrate oxygens are O^{18}-enriched.[112]

Although various explanations have been offered of the role of sulfuric acid in the nitration reaction, there is no reason to believe that it performs any other useful function than that of lowering the activity of water. This view is supported by the knowledge that cellulose can be nitrated equally well by nitric acid containing other dehydrating agents such as nitric anhydride, phosphoric anhydride, or acetic anhydride. In fact, cellulose can be nitrated by nitric acid alone (as was shown above), and, if steps are taken to remove the water formed in the reaction, as is the case when cellulose is treated with HNO_3 vapors under reduced pressure, products with 13.6% N can readily be obtained.[49]

Two general concepts have been advanced to explain the manner in which nitration proceeds in cellulose fibers.[113] According to the first of these concepts, the nitration reagent penetrates between the cellulose micelles and nitration proceeds progressively from the outside to the interior of the micelle

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[105] E. Berl and G. Rueff, *Cellulosechemie*, **14**, 97 (1933).

[106] R. C. Farmer, *J. Soc. Chem. Ind.* (London), **50**, 75T (1931).

[107] G. M. Bennett, J. C. D. Brand, and G. Williams, *J. Chem. Soc.*, **1946**, 869.

[108] F. W. Westheimer and M. S. Kharasch, *J. Am. Chem. Soc.*, **68**, 1871 (1946).

[109] G. Williams and A. M. Lowen, *J. Chem. Soc.*, **1950**, 3312.

[110] A. M. Lowen, M. A. Murray, and G. Williams, *J. Chem. Soc.*, **1950**, 3318.

[111] S. Israelashvili, *Nature*, **165**, 686 (1950).

[112] R. Klein and M. Mentser, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

[113] K. Fabel, *Nitrocellulose*, **11**, 223 (1940); **12**, 3 (1941).

(micellar heterogeneous reaction). The second concept, which has received widest acceptance, suggests that the nitration reagent penetrates uniformly into all parts of the cellulose fiber and all the molecules are nitrated at approximately the same time (homogeneous or permutoid reaction).

On the basis of x-ray examination of the structure of different specimens of nitrocellulose, Herzog and von Náray-Szabó,[114] and von Susich[115] claimed that all nitrocelluloses (below the trinitrate) are made up of mixtures of cellulose trinitrate and unchanged cellulose, and they suggested that the nitration of cellulose is a heterogeneous reaction. Hess and Trogus,[99,116] who have been the chief supporters of this theory, expressed the further belief that all esterification reactions of cellulose, including nitration, are micellar heterogeneous and are not of the homogeneous type. Sakurada and coworkers[117,118] proposed the following equation to cover all micellar heterogeneous reactions including cellulose nitration:

$$x = kz^m \tag{1}$$

in which x = amount of cellulose reacted, z = reaction time, and k and m = constants (see Section A of this Chapter IX). Chemical and x-ray analyses confirm, in their opinion, the view that the kinetics of cellulose nitration are determined by the velocity of diffusion rather than by the velocity of nitration. Tomonari[119] has claimed that the mechanism of the reaction is dependent on the composition of the mixed acid. With mixed acid very low in water content, the reaction is micellar heterogeneous because the rate of nitration is greater than the rate of diffusion; with acid mixes of high water content, the reaction approaches the permutoid type because of the greater speed of diffusion. Chédin and Tribot[120] concluded from a study of nitration rates that the reaction is made up of a fast reaction with readily available OH groups on the surface and a slow reaction with OH groups in the interior of micelles.

The overwhelming mass of evidence on this subject favors the permutoid theory of cellulose nitration. This evidence includes the conclusion, based on the work of Berl and coworkers[86] and others,[87,88] that an equilibrium exists between the nitrating medium and the nitrocellulose over a large range of composition. Despite the fact that equilibrium may be reached slowly when proceeding from a higher to a lower nitrogen content, the final nitrogen content is independent of time and can be changed to a higher or lower constant value by immersion in another mixed acid. The existence of this equilibrium is in harmony with the permutoid theory of nitration only.

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[114] R. O. Herzog and S. von Náray-Szabó, *Z. physik. Chem.*, **130,** 616 (1927).

[115] S. von Náray-Szabó and G. von Susich, *Z. physik. Chem.*, **134,** 264 (1928).

[116] K. Hess and C. Trogus, *Z. physik. Chem.*, **B15,** 157 (1931).

[117] I. Sakurada and M. Shojino, *J. Soc. Chem. Ind., Japan*, **35,** Suppl. binding, 287 (1932); **36,** Suppl. binding, 306 (1933).

[118] T. Nakashima, H. Nakahara, and I. Sakurada, *J. Soc. Chem. Ind., Japan*, **39,** Suppl. binding, 51 (1936).

[119] T. Tomonari, *J. Soc. Chem. Ind., Japan*, **37,** Suppl. binding, 478, 654, 772, 775 (1934); **38,** Suppl. binding, 58, 62 (1935).

[120] J. Chédin and A. Tribot, *Mém. services chim. état (Paris)*, **31,** 128 (1944).

Opposition to the micellar heterogeneous theory of cellulose nitration has also resulted from the failure to find any appreciable amount of unchanged cellulose in the examination of hundreds of nitrocellulose samples.[121] In other fractionation experiments with numerous nitrocellulose specimens, none of the fractions varied more than 0.3% in nitrogen content from the starting material; also no evidence was obtained of the presence of cellulose trinitrate in any of the samples.[101] Adam[122] has shown that nitrocellulose solutions spread to form monomolecular films of nitrocellulose on 2 *N* NaOH solution. In discussing these results, Miles[101] has pointed out that, if nitrocelluloses are constituted as claimed by Hess and Trogus,[116] either the micelle must solvate or disperse as such, in which case it seems impossible to account for the spreading to the thickness of one molecule; or the cellulose trinitrate must separate from the cellulose core since there is no reason for believing that the cellulose would disperse. If the latter case were true, only the cellulose trinitrate would spread and the measured film area for nitrocellulose of 10.4% N would be 35% less than was actually found, an error which could hardly be undetected.

Miles and Craik[101,102] examined by x-ray diffraction methods a series of nitrocelluloses, prepared with various HNO_3–H_2SO_4–H_2O mixtures, and the corresponding denitrated products. They divided the products into three classes depending on the position on the diagram (Fig. 7) of the mixed acid from which they were prepared: (I) N content less than 7.5%, fiber structure unimpaired, insoluble in all organic solvents; (II) N content 7.5–10.5%, fiber structure more or less impaired, swell or dissolve in acetone; (III) N content over 10.5%, fibrous, dissolve completely in acetone, comprise all technical nitrocelluloses. Miles and Craik were unable to confirm the conclusion of Herzog and coworkers that nitrocelluloses are to be regarded as mixtures of cellulose trinitrate and unchanged cellulose.

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[121] H. Brunswig, *Z. ges. Schiess- u. Sprengstoffw.*, **23**, 337, 384 (1928).
[122] N. K. Adam, *Trans. Faraday Soc.*, **29**, 95 (1933).

To account for their results, Miles and Craik presented the following picture of cellulose nitration. In the first stage of nitration (Class I) only the diffractions of almost completely mercerized cellulose were observed, and they therefore suggested that the OH groups in the "inner surface" of the fiber were nitrated while those in the interior of the micelles were not nitrated; that is, the reaction is heterogeneous. With a more concentrated nitration mixture, a greater area of the surface was affected so that in nitrations of Class II the number of unchanged cellulose chains was too small for definite diffraction and the micellar arrangement was almost entirely broken down. In Class III, the swelling and micellar disarrangement decreased as the concentration of the acid increased. With increase in concentration of the acid, the number of nitrate groups introduced increased, but with only approximate regularity, so that definite crystallization was difficult at first but became less so with increasing substitution, until at about 12.8% N the cellulose trinitrate diagram appeared. The essential feature of this picture is that in nitrations of Classes II and III the nitrate groups are so distributed among the chain molecules that there is little likelihood of any one molecule being completely nitrated to the trinitrate before the other molecules; that is, the reaction is permutoid.

Miles[101] also pointed out that Hess and Trogus[116] based their belief that cellulose nitration is a micellar heterogeneous reaction on the examination of nitrocelluloses (7 to 13% N) prepared by the somewhat unusual procedure of nitrating ramie for various periods (1 to 480 min.) with a single anhydrous nitrating mixture containing 29.7% HNO_3 and 70.3% H_2SO_4. It seems doubtful that the examination of these nitrocelluloses would give information of much value about the nature of the reaction which takes place in commercial nitration, because in the latter case the reaction is carried out practically to completion and the nitrogen content is controlled primarily by the mixed acid composition and not by the reaction time.

In an extension of the work of Demougin and Bonnet,[104] Chédin and Tribot[91,93,95] investigated the composition of the spent nitrating acid removed by vigorous centrifuging and that retained in the nitrated fibers. They found that the retained acid is richer in HNO_3. They concluded from their extensive results that the crystalline portions of cellulose fibers are more readily penetrated by the small planar HNO_3 molecules than by the relatively large H_2SO_4 molecules. At the end of nitration, the degree of hydration of HNO_3 in the crystalline areas of the fibers is the same as that in the noncrystalline areas. According to Chédin and Tribot, this explains why the degree of nitration is uniform throughout the fibers at equilibrium.

Kagawa[123] determined that the total heat liberated on nitration of cellulose to 10.4% N is 77.5 calories per gram of cellulose. From this he computed that the actual heat of nitration of cellulose is 2.11 kcal. per mole of OH nitrated. In a similar investigation, Calvet[124] obtained a value for the heat of nitration of 2.05 kcal. per mole of OH nitrated. Jessup and Prosen[125] derived the following equations expressing heat of combustion (ΔH_c^0) and heat of formation (ΔH_f^0) of nitrocellulose as functions of nitrogen content:

$$\Delta H_c^0 = 4176.70 + 14126f' \text{ cal./g. nitrocellulose}$$

$$\Delta H_f^0 = -5896.88 + 26178f' \text{ cal./g. nitrocellulose}$$

f' = mass fraction of nitrogen in nitrocellulose (corrected for impurity in the nitrocellulose) in the range 0.115 to 0.135.

(5) *Stability and Stabilization*

A point of major importance in the chemistry of nitrocellulose is the fact that its usefulness in explosives or in ordinary articles of commerce depends a great deal upon its stability, that is, upon its ability to resist decomposition after long periods of time under various conditions. Thus, in guncotton, the decomposition of unstable nitrocellulose during storage can accelerate to the point at which the nitrocellulose will explode. The use of unstable nitrocellulose will result in gradual embrittlement and disintegration of films; in coated cloth (artificial leather) the coatings will embrittle, then crack and peel off; in lacquers the instability will cause corrosion of the metal on which the lacquer has been applied.[30,126]

In the first years of the development of the manufacture of nitrocellulose, which were devoted almost exclusively to the production of guncotton, a number of disastrous explosions occurred which were caused by the instability of the product. The search for the causes of this instability resulted in the discovery by Abel,[127] nearly 100 years ago, that retention of traces of the nitrating acid by the nitrocellulose can cause instability. Wiggam[128] showed that the stability of nitrocellulose is lowered to an extent dependent upon the amount of acid remaining absorbed. The formation of sulfuric acid esters of nitrocellulose during nitration was recognized early in this century.[129,130] Hake and Lewis[131] were among the first to suggest that the instability of nitrocellulose can also be caused by the gradual splitting off of the unstable sulfate groups. The formation of these sulfuric acid esters, and hence the stability, was found to vary with the composition of the nitrating acid mixture. The combined sulfate content was found to increase with increase in (a) nitration time,[130] (b) $H_2SO_4:HNO_3$ ratio in the mixed acid,[130,132,133] and (c) nitrosylsulfuric acid content of the mixed acid.[66] An increase in the water content of the mixed acid increased the stability of the nitrocellulose produced.[66,134] It is interesting to note that when the formation of sulfuric acid esters of cellulose is avoided, as in nitration with HNO_3 vapors, nitrocelluloses of high stability are obtained by merely washing the products with cold water.[49]

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[123] I. Kagawa, *J. Soc. Chem. Ind., Japan*, **42**, Suppl. binding, 236 (1939).

[124] E. Calvet, *Mém. services chim. état (Paris)*, **34**, 179 (1948).

[125] R. S. Jessup and E. J. Prosen, *J. Research Natl. Bur. Standards*, **44**, 387 (1950).

[126] J. B. Wiesel, *Paint, Oil Chem. Rev.*, **80**, No. 10, 8 (1925).

[127] F. Abel, Brit. Patent 1102 (1865); see also E. C. Worden, *Technology of Cellulose Esters*, Vol. I, Part 3, p. 1604 *et seq.*, E. C. Worden, Millburn, N. J., 1921.

[128] D. R. Wiggam, *J. Phys. Chem.*, **35**, 536 (1931).

Various methods have been developed to improve the stability of nitrocellulose. Abel undertook the study and manufacture of guncotton for the British Government in 1863. Following his discovery of the effect of retained acid on stability, he found that pulping of guncotton in a paper beater considerably reduced the fiber length of the nitrated cotton and thus permitted ready removal of the retained acid by washing.[127] In the Abel process, the washing was carried out with alkaline water in order to bring the nitrocellulose to neutrality as soon as possible.

Reeves and Giddens[135] found that treatment of incompletely purified nitrocellulose with cold dilute aqueous ammonia caused a marked improvement in stability tests without reducing the appreciable sulfate content of the original nitrocellulose. They attributed the improvement in stability to the neutralization of sulfuric acid trapped within the fibers. They also observed that nitrocellulose which had been stabilized by long boiling and beating treatments was not further improved in stability by their ammonia treatment. There is reluctance in the nitrocellulose industry to rely on ammonia neutralization of bound sulfate groups, because it is

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[129] C. F. Cross, E. J. Bevan, and R. L. Jenks, *Ber.*, **34**, 2496 (1901).

[130] C. N. Hake and M. Bell, *J. Soc. Chem. Ind.* (London), **28**, 457 (1909).

[131] C. N. Hake and R. J. Lewis, *J. Soc. Chem. Ind.* (London), **24**, 374, 914 (1905).

[132] A. Hervé, *Le Moniteur Scientifique Quesneville*, [5], **8**, 193 (1918).

[133] L. Brissaud, *Mém. poudres*, **26**, 158 (1934–5).

[134] T. Tomonari, *J. Soc. Chem. Ind., Japan*, **37**, Suppl. binding, 511 (1934); **38**, Suppl. binding, 326 (1935).

[135] R. E. Reeves and J. E. Giddens, *Ind. Eng. Chem.*, **39**, 1303, 1306 (1947); (to the U. S. Secretary of Agriculture), U. S. Patents 2,404,887 (July 30, 1946) and 2,471,583 (May 31, 1949); *Chem. Abstracts*, **43**, 5950 (1949).

feared that these groups will hydrolyze in the course of time, leading to acidity and rapid decomposition.

According to Mohr,[136] squeezing water-wet nitrocellulose in a hydraulic press aids in the removal of retained acid and thereby improves the stability.

The foundation for an important part of the stabilization process was laid in 1906 when Robertson[137] discovered that the unstable sulfuric acid esters of nitrocellulose are more readily decomposed by steeping the nitrocellulose in boiling water while it still retains a small amount of mixed acid, than by Abel's treatment with boiling alkaline water. At equal concentrations the stabilizing action of the following acids in the wash water decreases in this order: HNO_3, HCl, and H_2SO_4.[138] According to Milliken,[139] the stabilization process can be shortened appreciably by heating the nitrocellulose in water at above 100°C. under pressure, for example, at 116°C. under a hydrostatic pressure of 15 lb./sq. in. If nitrocellulose which has been stabilized by an acid boil is treated with water containing $CaCO_3$ (for example, hard water), a further improvement in stability results.[140–142] This behavior is explained by the fact that the residual combined H_2SO_4 in nitrocellulose exists largely in the form $R_{cell}O \cdot SO_2OH$ which is readily hydrolyzed by water or acids but which becomes $R_{cell}O \cdot SO_2OM$ in presence of inorganic bases.[143] This salt is stable to inorganic bases[143] and even to dilute acids.[141] Kridel and Rogers[144] stabilized nitrocelluloses containing relatively large amounts of combined sulfate (0.3 to 3.0%) by steeping them in an aqueous solution of an alkali metal hydroxide or alkali metal salt of a weak acid, such as sodium acetate.

Kullgren[145–147] carried out an extensive study of the combined sulfate groups in nitrocellulose. He found that the cation exchange which occurs when nitrocellulose is suspended in salt solutions is due to $R_{cell}O \cdot SO_2OH$

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[136] R. Mohr, *Makromol. Chem.*, **4,** 55 (1949).

[137] R. Robertson, *J. Soc. Chem. Ind.* (London), **25,** 624 (1906).

[138] P. Demougin and M. Landon, *Mém. poudres*, **27,** 182 (1937).

[139] M. G. Milliken (to Hercules Powder Co.), U. S. Patents 2,103,592 (Dec. 28, 1937) and 2,103,593 (Dec. 28, 1937); *Chem. Abstracts*, **32,** 1932 (1938).

[140] J. Goujon, *Mém. artillerie française*, **8,** 837 (1929).

[141] M. Landon, *Mém. poudres*, **27,** 190 (1937).

[142] A. Breguet and A. Caille, *Bull. soc. chim.*, [4], **35,** 680 (1924).

[143] J. F. Briggs, *J. Soc. Chem. Ind.* (London), **25,** 626 (1906).

[144] D. J. Kridel and W. J. Rogers (to Eastman Kodak Co.), U S. Patent 2,604,471 (July 22, 1952); *Chem. Abstracts*, **46,** 9844 (1952).

[145] C. Kullgren, *Svensk Kem. Tid.*, **53,** 233 (1941); *Chem. Abstracts*, **36,** 262 (1942).

[146] C. Kullgren, *Ing. Vetenskaps Akad., Handl.*, No. **165,** 5 (1942); *Chem. Abstracts*, **41,** 5714 (1947).

[147] C. Kullgren, *Svensk Kem. Tid.*, **56,** 221 (1944); *Chem. Abstracts*, **40,** 2630 (1946).

groups. Not all of the combined H_2SO_4 is present in this form. Some of it is present as the neutral sulfate—$R_{cell}O \cdot SO_2OR_{cell}$, which is decomposed very slowly in boiling water and somewhat more readily if the boiling water is acidified slightly. Nitrocellulose which has not been stabilized by boiling evolves acid even after long-continued washing; this is due to the slow decomposition of combined sulfate groups. Kullgren interpreted this behavior to indicate that the hydrolysis of $R_{cell}O \cdot SO_2OH$ groups in unstabilized nitrocellulose, which occurs when the latter is stored in water, results in some of these groups being converted to $R_{cell}OH$ and others to $R_{cell}O \cdot SO_2OR_{cell}$. This postulated formation of neutral sulfate ester groups in the presence of excess water is improbable. Regardless of the mechanism involved, Kullgren's contention that the stabilization treatment should be carried out as soon as the nitrating acids have been removed is probably correct.

Improvement in the stability of nitrocellulose has been effected by extraction with alcohols under various conditions,[148–153] including the commercial dehydration of nitrocellulose with ethyl alcohol.[30] Berl and Delpy[154] removed material of low stability from nitrocellulose by alcohol extraction and suggested that it was highly degraded nitrocellulose Kullgren[146] found that H_2SO_4 is formed more rapidly on treatment of nitrocellulose with methanol than with water. His results indicated that the methanol treatment decomposes both $R_{cell}O \cdot SO_2OH$ and $R_{cell}O \cdot SO_2OR_{cell}$ groups. Chédin and Tribot[155] dissolved in acetone a nitrocellulose which had been thoroughly washed with cold water after nitration and then precipitated the nitrocellulose by pouring the solution into water. This treatment reduced the combined H_2SO_4 content from 0.7% to 0.1%.

Parallel with the development of stabilization and purification treatments, there has occurred the development of materials (stabilizers) to be incorporated with nitrocellulose plastics, coatings, and propellant powders in order to prolong their life by absorbing the products of nitrocellulose

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[148] H. Muraour, *Bull. soc. chim.*, [4], **51**, 1089 (1932).

[149] F. Langenscheidt, *Z. ges. Schiess- u. Sprengstoffw.*, **9**, 54 (1914).

[150] G. Centola, *Ann. chim. appplicata*, **31**, 539 (1941); *Chem. Abstracts*, **39**, 1539 (1945).

[151] R. W. Scharf, U. S. Dept. of Commerce, Washington 25, D. C., OTS, PB Rept. 51091 (1942).

[152] Sadayoshi Watanabe, *J. Soc. Chem. Ind., Japan*, **46**, 505 (1943); *Chem. Abstracts*, **43**, 1965 (1949).

[153] L. Brissaud, *Mém. poudres*, **31**, 81 (1949).

[154] E. Berl and M. Delpy, *Z. ges. Schiess- u. Sprengstoffw.*, **8**, 129 (1913).

[155] J. Chédin and A. Tribot, *Mém. services chim. état* (*Paris*), **32**, 157 (1945); *Chem. Abstracts*, **42**, 4746 (1948).

decomposition.[156] Ideally, the stabilizer should be nonvolatile, completely compatible with the nitrocellulose, and chemically inert toward it. Basic inorganic compounds, such as $CaCO_3$, were among the first materials used as stabilizers. It should be noted, however, that $CaCO_3$ will react with nitrocellulose under certain conditions and actually reduce its stability.[157,158]

Many organic compounds have been proposed and evaluated as stabilizers for nitrocellulose.[159-170] Compounds most widely used for this purpose are weak organic bases and include diphenylamine, *sym*-diethyldiphenylurea (*N*,*N*′-diethylcarbanilide; Centralite I), and 1,1-diphenylurea (acardite). According to Gilbert,[171] the color stability of nitrocellulose lacquers and base solutions is improved by incorporating in the nitrocellulose a small amount (0.01 to 0.20% calculated as phosphoric acid) of phosphoric, citric, or tartaric acid.

When considering the possibility of adding a "stabilizer" to nitrocellulose, it should always be remembered that no known substance can reduce the inherent, very slow rate of spontaneous degradation. On the contrary, many substances that have been proposed as stabilizers, such as the organic nitrogen compounds mentioned above, urea, and calcium carbonate,[157,158] actually increase the rate of decomposition and are therefore deleterious in most applications. For example, phosphoric acid is slightly harmful (Chapter X-A, Fig. 16). However, phosphoric acid is much less harmful than traces of base derived from hard water or ingredients of a lacquer formulation. Therefore, it is sometimes advisable to use a small amount of phosphoric acid.

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[156] A. Marshall, *Explosives*, P. Blakiston's Son & Co., New York, Vol. II, 1917, p. 640; Vol. III, 1932, p. 210. A review.

[157] A. Koehler and M. Marqueyrol, *Mém. poudres*, **23**, 11 (1928).

[158] P. Demougin, *Mém. poudres*, **26**, 119 (1934–5).

[159] M. Marqueyrol, *Mém. poudres*, **23**, 158 (1928).

[160] M. Tonegutti, *Atti V congr. nazl. chim. pura ed applicata, Rome*, **1935**, Part II, 899 (1936); *Chem. Abstracts*, **31**, 8198 (1937).

[161] H. Muraour, *Bull. soc. chim.*, [5], **3**, 2240 (1936).

[162] R. Dalbert, *Mém. poudres*, **27**, 117 (1937); **28**, 147 (1938).

[163] T. Urbanski, B. Kwiatowski, and W. Miladowski, *Z. ges. Schiess- u. Sprengstoffw.*, **32**, 1, 29, 57, 85 (1937).

[164] T. Urbanski and W. Miladowski, *Z. ges. Schiess- u. Sprengstoffw.*, **33**, 247 (1938).

[165] H. Ficheroulle, *Mém. poudres*, **31**, 167 (1949).

[166] V. R. Grassie, L. Mitchell, J. M. Pepper, and C. B. Purves, *Can. J. Research*, **28B**, 468 (1950).

[167] L. Médard, *Mém. poudres*, **32**, 305 (1950).

[168] W. A. Schroeder, B. Keilin, and R. M. Lemmon, *Ind. Eng. Chem.*, **43**, 939 (1951).

[169] J. A. Wyler and R. N. Boyd (to Trojan Powder Co.), U. S. Patent 2,297,734 (Oct. 6. 1942); *Chem. Abstracts*, **37**, 1622 (1943).

[170] D. R. Swan and J. M. Calhoun (to Eastman Kodak Co.), U. S. Patents 2,311,098 (Feb. 16, 1943); *Chem. Abstracts*, **37**, 4316 (1943); 2,378,594 (June 19, 1945); *Chem. Abstracts*, **39**, 4222 (1945); and 2,407,209 (Sept. 3, 1946); *Chem. Abstracts*, **40**, 7625 (1946).

[171] C. B. Gilbert (to Hercules Powder Co.), U. S. Patent 2,260,248 (Oct. 21, 1941); *Chem. Abstracts*, **36**, 903 (1942).

One exception to the general rule that no "stabilizer" should be used is furnished by smokeless powder. In this case, the material is handled in massive quantities and may be stored for decades. There is little chance for the escape of any nitric acid that may accumulate, and it is desirable to add substances that will react with the nitric acid, and yet are not basic enough to catalyze decomposition. The following discussion should be considered as being applicable only to smokeless powder problems.

It is apparent from the results of many investigations on the mechanism of decomposition of nitrocellulose that this decomposition takes place in two stages. In the first stage, the reaction is relatively slow; in the second stage, the initial decomposition products react with the nitrocellulose, and the reaction becomes autocatalytic and therefore accelerates rapidly. If the products of decomposition in the first stage are removed as rapidly as formed (for example, by a stabilizer), the reactions of the second stage are prevented, and the decomposition is held down to a relatively slow rate.[159,172]

Since nitrocellulose decomposes rather slowly at room temperature, a wide variety of stability tests have been devised in which the nitrocellulose is heated to accelerate decomposition; the results thus give an advance indication of the stability behavior of a particular lot of nitrocellulose on storage.[173–175] Wide differences in the bases of these tests have led to differences in the interpretation of stability behavior.

In the decomposition of nitrocellulose at room temperature, hydrolysis is caused by traces of acid which have not been completely washed out or which result from the decomposition of unstable ester groups. The hydrolysis results in scission of the cellulose chain and the splitting off of nitrate groups. If the nitrogen oxide decomposition products are removed

[172] G. de Bruin, *Études sur la décomposition spontanée de la poudre sans fumée, II*, Communiqué de la Soc. Anon. Fabriques Néerlandaises D'Explosifs, No. 2, Amsterdam, May, 1924.

[173] A. Marshall, *Explosives*, P. Blakiston's Son & Co., Philadelphia, Vol. II, 1917, p. 644, and Vol. III, 1932, p. 213.

[174] D. R. Wiggam and E. S. Goodyear, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 73 (1932).

[175] M. Tonegutti and E. Brandimarte, *Z. ges. Schiess- u. Sprengstoffw.*, **35**, 52, 76, 100, 124, 145, 169 (1940).

as rapidly as formed (for example, by a stabilizer) and thereby are prevented from reacting with the nitrocellulose, the decomposition proceeds rather slowly and not with the increasing velocity that otherwise results.[176]

At elevated temperatures, another reaction takes place in the decomposition of nitrocellulose; this is the internal combustion of some of the anhydroglucose groups with resultant scission of the cellulose chain. If the nitrogen oxides are not removed, they form with the water present a solution of nitric and nitrous acids which comprises the medium for the following secondary reactions: (a) oxidation of glucose units, (b) hydrolysis of nitrate groups, and (c) hydrolytic scission of the cellulose chain.[177,178]

Moisture content plays an important part in the decomposition of nitrocellulose by hydrolysis. According to Muraour,[179] water exerts no action at 15° to 20°C. on suitably prepared nitrocellulose even after 20 to 30 years. At 50° to 75°C. in a humid atmosphere, the deterioration of nitrocellulose is rapid; the initial hydrolysis of the ester causes rapid decomposition of nitrocellulose. The action of HNO_3 on nitrocellulose is strongly dependent on its concentration. A decrease in the moisture content (but not to complete dryness) of smokeless powder containing even a trace of free acid may cause an increase in the rate of decomposition. A large amount of water dilutes the HNO_3 and thereby retards or completely stops the decomposition. A minimum concentration of HNO_3 is necessary to produce hydrolysis.

(6) Viscosity

The degree of polymerization (D.P.) of nitrocellulose is important in all of its uses. An increase in D.P. is usually favorable from the standpoint of physical properties, such as strength and flexibility. However, this increase in D.P. is also accompanied by an increase in the viscosity of solutions. A high D.P. therefore makes it difficult to handle nitrocellulose solutions, as, for example, the application of lacquers. Thus, in actual use, it is necessary to make a compromise between favorable physical properties and low viscosity in solution.

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[176] H. Muraour, *Chimie & Industrie*, **20**, 610 (1928); *Bull. soc. chim.*, [4], **47**, 1259 (1930).

[177] J. Desmaroux, *Compt. rend.*, **194**, 1649 (1932); **196**, 1394 (1933).

[178] J. Desmaroux, R. Vandoni, L. Brissaud, and T. Petitpas, *Mém. poudres*, **29**, 134 (1939).

[179] H. Muraour, *Bull. soc. chim.*, [4], **49**, 276 (1931); **51**, 1094 (1932); see also G. de Bruin and P. F. M. de Pauw, *Études sur la décomposition spontanée de la poudre sans fumée, IV*, Communiqué de la Soc. Anon. Fabriques Néerlandaises D'Explosifs, No. 4, Amsterdam, Oct., 1925.

The utility of viscosity measurements for the characterization of nitrocellulose was recognized long before there was wide acceptance of the fact that nitrocellulose is a high polymer and that solution viscosity is connected with D.P. Consequently, a number of empirical tests were devised to characterize viscosity (see Chapter XII and also Appendix for a comparison of various tests and D.P.), and attention was directed to methods for the control of viscosity.

The viscosity of nitrocellulose may be influenced by a number of factors including the viscosity of the original cellulose[180,181] and the nitration conditions.[182] An increase in the $H_2SO_4:HNO_3$ ratio or a reduction in the ratio of mixed acid to cellulose (in the range from 80:1 to 30:1) will result in nitrocellulose of lower viscosity.[30] Viscosity will also be reduced by an increase in nitration time,[30,183] nitration temperature,[30,184] or in the nitrosylsulfuric acid content of the mixed acid.[30] The use of HNO_3–H_3PO_4–P_2O_5 mixtures for nitration yields nitrocelluloses of very high viscosity. This procedure is believed to cause less decrease in molecular chain length (and thus, D.P.) than any other nitration method[68–70] and, as indicated previously, is frequently used in scientific work in the determination of D.P. and the distribution of molecular weights of the original cellulose (see Chapter X-D).

For certain types of nitrocellulose the viscosity can be adequately regulated by controlling the various factors mentioned above. On the other hand, a considerable proportion of the nitrocellulose manufactured is of the low-viscosity type designed to meet the need of the lacquer industry for increasing the concentration of nitrocellulose in lacquers without increasing their viscosity. The increase in nitrocellulose concentration permits the deposition of a thicker lacquer film in a single application and reduces the cost. Processes have been developed for reducing the viscosity of cellulose for the production of low-viscosity nitrocelluloses.[14] However, most of the low-viscosity nitrocelluloses on the market are made by processes which include some special viscosity-reducing treatment after nitration.[185–187] The nitrocellulose may be treated with hot dilute solutions of

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[180] F. Olsen, *Ind. Eng. Chem.*, **21**, 354 (1929).

[181] H. Aaronson, U. S. Dept. of Commerce, Washington 25, D. C., OTS, PB Rept. 53806 (1932).

[182] A. Tribot and A. Marsaudon, *Mém. services chim. état* (*Paris*), **32**, 145 (1945).

[183] K. Atsuki and M. Ishiwara, *Proc. Imp. Acad.* (*Tokyo*), **4**, 386 (1928).

[184] K. Atsuki and M. Ishiwara, *J. Soc. Chem. Ind., Japan*, **31**, Suppl. binding, 268 (1928).

[185] R. Gabillion, *Rev. gén. mat. plastiques*, **7**, 259, 323 (1931); *Chem. Abstracts*, **25**, 5555 (1931).

acids, bases,[188,189] or oxidizing agents[190,191] or it may be digested in water under pressure.[192,193] The rate of viscosity reduction on heating nitrocellulose in water at 132°C. under pressure[192] is shown in Figure 10.

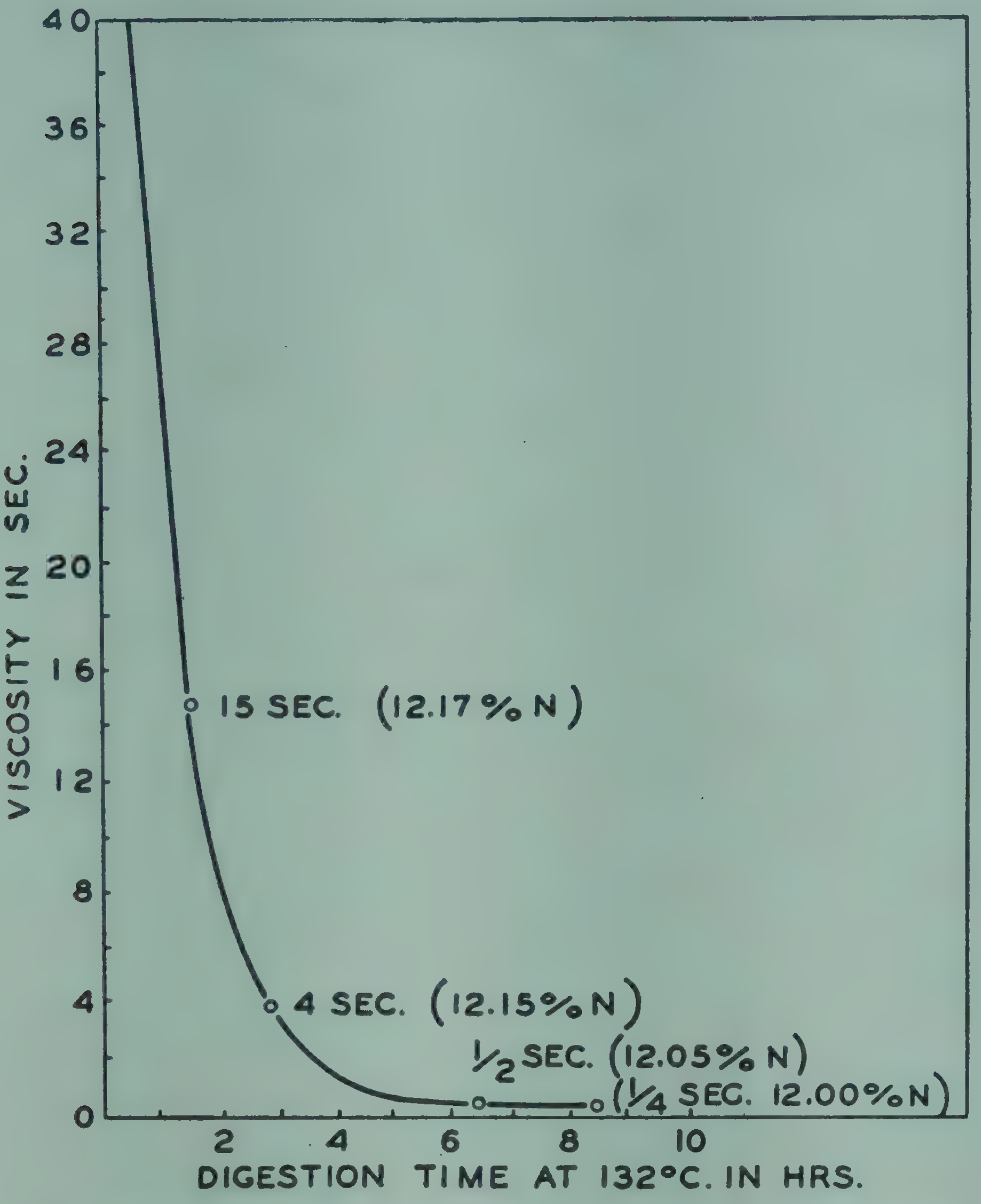

Fig. 10. Rate of viscosity reduction of nitrocellulose on digestion in water at 132°C. (Milliken[192]). The viscosities were determined in 12.2% solution by the Hercules method.[5]

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[186] C. Stark, *Kunststoffe*, **21**, 151, 201 (1931); *Chem. Abstracts*, **25**, 5760 (1931).

[187] M. Pavlik, *Congr. chim. ind., Compt. rend. 17e Congr., Paris*, Sept.-Oct., **1937**, 1058; *Chem. Abstracts*, **32**, 7719 (1938).

[188] S. B. Luce (to Monsanto Chemical Co.), U. S. Patent 2,467,324 (April 12, 1949); *Chem. Abstracts*, **43**, 4853 (1949).

[189] N. Moreau and Y. Lacroix, *Mém. poudres*, **32**, 443 (1950).

[190] K. Thinius (to Deutsche Celluloid-Fabrik), U. S. Patent 2,104,957 (Jan. 11, 1938); *Chem. Abstracts*, **32**, 2352 (1938).

[191] J. R. Buckley (to Canadian Industries Ltd.), Canadian Patent 442,207 (June 17, 1947); *Chem. Abstracts*, **41**, 6718 (1947).

[192] M. G. Milliken, *Ind. Eng. Chem.*, **22**, 326 (1930).

[193] M. G. Milliken (to Hercules Powder Co.), U. S. Patents 1,818,733 (Aug. 11, 1931); 1,911,201 (May 30, 1933).

If the viscosity data in Figure 10 are converted to intrinsic fluidities (by means of the graph given in the Appendix) and the latter are plotted against time, a straight-line relation is found. This behavior is consistent with the idea expressed in Section C of Chapter III that random scission of the nitrocellulose chain molecules occurs in the viscosity reduction process.

Lawton and Nason[194] found that exposure to ultraviolet light causes a decrease in the intrinsic viscosity of nitrocellulose. The viscosity reduction is less in a nitrogen atmosphere than in air or oxygen.

(b) COMMERCIAL MANUFACTURE OF NITROCELLULOSE[195,196]

In the direct dipping process, which was used in the early days of nitrocellulose manufacture, the cotton was dipped in the mixed acid and, after nitration was complete, the nitrated product was transferred by hand to a centrifuge where the spent acid was removed. In a later development, nitration was carried out directly in a centrifuge which was rotated slowly to cause circulation of the acid; when nitration was complete, the centrifuge was rotated more rapidly and the spent acid was removed. The nitrocellulose was then transferred with aluminum forks to washing tubs.[197]

The Thomson displacement process attained large-scale operation in England, where it was developed for the manufacture of guncotton. In this process, pans with perforated false bottoms are filled with mixed acid; then cotton is added and covered with a perforated plate so that the cotton is completely submerged. At the end of nitration, the spent acid is drained off slowly and is displaced at the same time with water. The advantages claimed for this process include: (a) low power consumption; (b) no moving parts, hence low investment in equipment; (c) low maintenance cost; and (d) practically complete recovery of all acid.[197,198]

The most widely used process is still the so-called mechanical dipper process,[199–203] which was developed many years ago by the du Pont Company. A sketch of a nitration building and equipment is shown in Figure 11. The dippers consist of cylindrical tanks made of an acid-resistant steel alloy and fitted with two stirrers. A pipe of large diameter, closed by a valve, leads from the bottom of the dipper to a centrifuge on the floor below.

[194] T. S. Lawton, Jr., and H. K. Nason, *Ind. Eng. Chem.*, **36**, 1128 (1944).

[195] G. Bonwitt, *Das Celluloid und seine Ersatzstoffe*, Union Deutsche Verlagsges., Berlin, 1933.

[196] K. Fabel, *Nitrocellulose; Herstellung und Eigenschaften*, Ferdinand Enke Verlag, Stuttgart, 1950, p. 91. See this reference, p. 74, for a review of patents on nitrocellulose manufacture which supplements the list given by Faust (ref. 3).

[197] F. L. Nathan, *J. Soc. Chem. Ind.* (*London*), **28**, 177 (1909).

[198] Anon., *Chem. & Met. Eng.*, **50**, No. 10, 130 (1943).

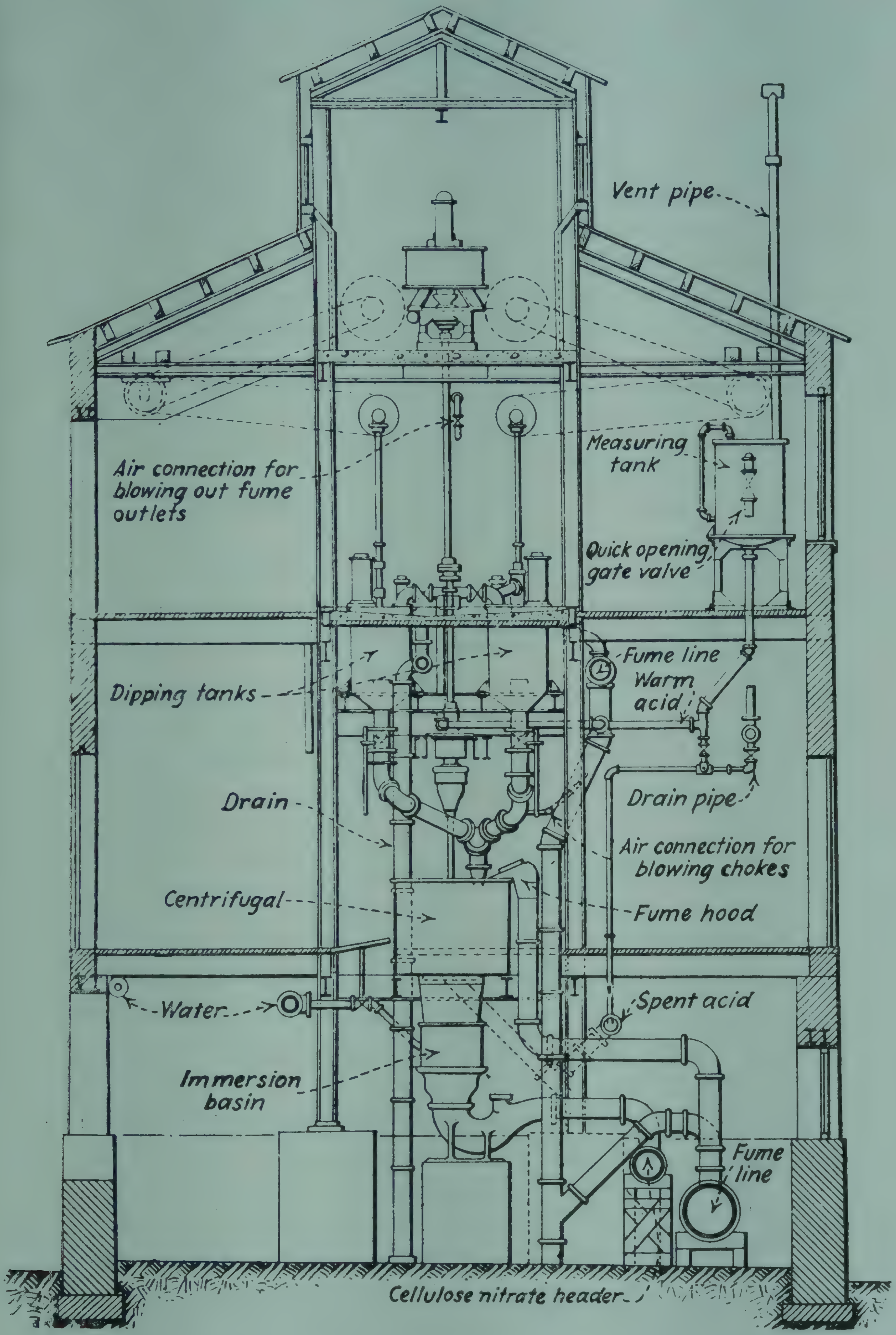
Vent pipe
Measuring tank
Air connection for blowing out fume outlets
Quick opening gate valve
Fume line
Warm acid
Dipping tanks
Drain
Drain pipe
Air connection for blowing chokes
Centrifugal
Fume hood
Water
Spent acid
Immersion basin
Fume line
Cellulose nitrate header

Fig. 11. Nitrating building and equipment for the mechanical dipper process of nitration (du Pont[199]).

Four dippers and one centrifuge form a unit in this process. The cellulose to be nitrated, in suitable physical form, is dried to a moisture content of less than 1%. The drying operation is important because excessive moisture in the cellulose results in: (a) lower degree of nitration than planned due to dilution of the mixed acid, (b) poor solubility because of irregular nitration, and (c) temperature rise on dipping which causes disintegration of fibers and loss in yield.[30,199] About 1600 lb. of mixed acid of selected composition is charged at a definite temperature into the dipper from a measuring tank, and about 30 lb. of dried cellulose is then added. The latter is quickly wetted and submerged as a result of the mechanical agitation. After nitration has continued about 30 min., the bottom valve is opened and the mixture of spent acid and nitrocellulose is discharged directly into the centrifuge, where most of the spent acid is removed in about 5 min. In general, about 1 lb. of acid is retained by each pound of nitrocellulose in the centrifuge. The nitrocellulose is discharged through an opening in the bottom of the centrifuge into a volume of water which thoroughly drowns the nitrocellulose and is large enough to prevent any appreciable rise in temperature. The nitrocellulose is then floated through a pipe (nitrocellulose header) to the purification area. The spent acid leaving the centrifuge is accumulated and brought back to proper strength for re-use in nitration by the addition of strong nitric and sulfuric acids. This process yields a very uniform product because of the agitation during nitration and requires a minimum amount of manual labor.

Purification and stabilization of the nitrocellulose is carried out in large wooden tubs lined with chrome-steel sheet and fitted with agitators. These tubs, which can hold as much as 12,000 lb. of nitrocellulose, are also equipped with a perforated false bottom under which steam lines are uniformly distributed. After the nitrocellulose has been washed to a predetermined acidity, the tubs are filled with water which is heated to boiling by admitting live steam. This stabilization treatment may consist of one continuous boil or it may consist of a series of short boils with frequent changes of water. Depending on the type of nitrocellulose being manufactured, boiling and agitation are continued for 10 to 60 hrs.[204] For

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[199] J. R. du Pont, *Chem. & Met. Eng.*, **26**, 11 (1922).

[200] A. B. Nixon, *Hercules Mixer*, **8**, 55 (1926).

[201] E. P. Partridge, *Ind. Eng. Chem.*, **21**, 1044 (1929).

[202] L. Sheldon, U. S. Dept. of Commerce, Washington 25, D. C., OTS, PB Rept. 12662 (1945).

[203] E. F. Thoenges, *Manufacture of Cellulose Nitrate*, in P. H. Groggins, editor, *Unit Processes in Organic Synthesis*, 4th ed., McGraw-Hill, New York, 1952, pp. 648–650.

[204] C. G. Dunkle, U. S. Dept. of Commerce, Washington 25 D. C., OTS, PB Rept. 3055 (1941).

some types, the nitrocellulose is also pulped in machines similar to paper beaters in order to reduce the fibers to a fine state of division and to remove occluded acid. The nitrocellulose is then treated with dilute Na_2CO_3 solutions and finally washed to neutrality.

For certain industrial uses, such as the manufacture of high-grade plastics, nitrocellulose is often bleached to remove traces of color. The nitrocellulose may be bleached with a solution containing 2 lb. of $KMnO_4$ per 100 lb. of nitrocellulose and made slightly acid with H_2SO_4. When reduction of the permanganate is complete, the nitrocellulose is washed and the brown color removed by a solution of oxalic acid or SO_2. The nitrocellulose may also be bleached by a 30- to 60-min. treatment with a 1% solution of chlorine or bleaching powder. The nitrocellulose is then washed, treated with an antichlor, such as Na_2SO_3, to remove all traces of chlorine, and washed again.[199]

As was indicated previously, special treatment is required to produce the very low viscosity types of nitrocellulose required for lacquers. In early industrial practice, the usual procedure[186] involved batch digestion during which nitrocellulose suspended in water was heated under pressure in welded steel, brick-lined autoclaves holding 4000 lb. of nitrocellulose and 60,000 lb. of water per charge. With digesters of this size, difficulty was sometimes encountered in removing adequately the gases resulting from the slight denitration of nitrocellulose, and explosions occurred. These explosions were probably due to the entrainment of gases in the fibrous mass, which caused dry spots in the batch. A marked advance in this phase of nitrocellulose manufacture was achieved by Milliken[192–193] in the development of a continuous digester which avoids the hazards encountered in batch pressure digestion. In the continuous process, a suspension of purified nitrocellulose in water is fed by centrifugal pumps into a coiled, acid-resisting alloy tube 4 in. in diameter and 4000 ft. long (see Fig. 12), which is heated by a steam jacket for a distance at the entrance, heat-insulated along most of its length, and cooled by a water jacket for a distance near the exit end. To prevent flashing of the water in the coil, it is subjected to a back pressure by connecting the exit to a standpipe 200 ft. high. The rate of flow of the mixture and its temperature are controlled so that any practical degree of viscosity reduction can be uniformly maintained. The continuous digester is so designed that the small amounts of gas resulting from denitration move along the tube with the nitrocellulose from which they were evolved so that they have no opportunity to form gas pockets. The products of this treatment are very uniform as evidenced by their high solution clarity; their stability is also very good.

Practically all types of nitrocellulose are dehydrated before use. The loosely held water can be removed by draining or centrifuging. The wet nitrocellulose is then transferred to hydraulic presses where it is formed into cylindrical blocks with a pressure of about 250 lb./sq. in. Denatured ethyl alcohol is then forced through the block in the proportion of about 2 lb. of alcohol per pound of nitrocellulose. The excess alcohol is removed by applying a pressure of 3000 lb./sq. in. to the block. The compressed block, which now contains about 30% by weight of ethyl alcohol, is broken up and packed in steel drums for shipment. Commercial nitrocellulose has also been dehydrated with isopropyl alcohol or butyl alcohol for certain uses.

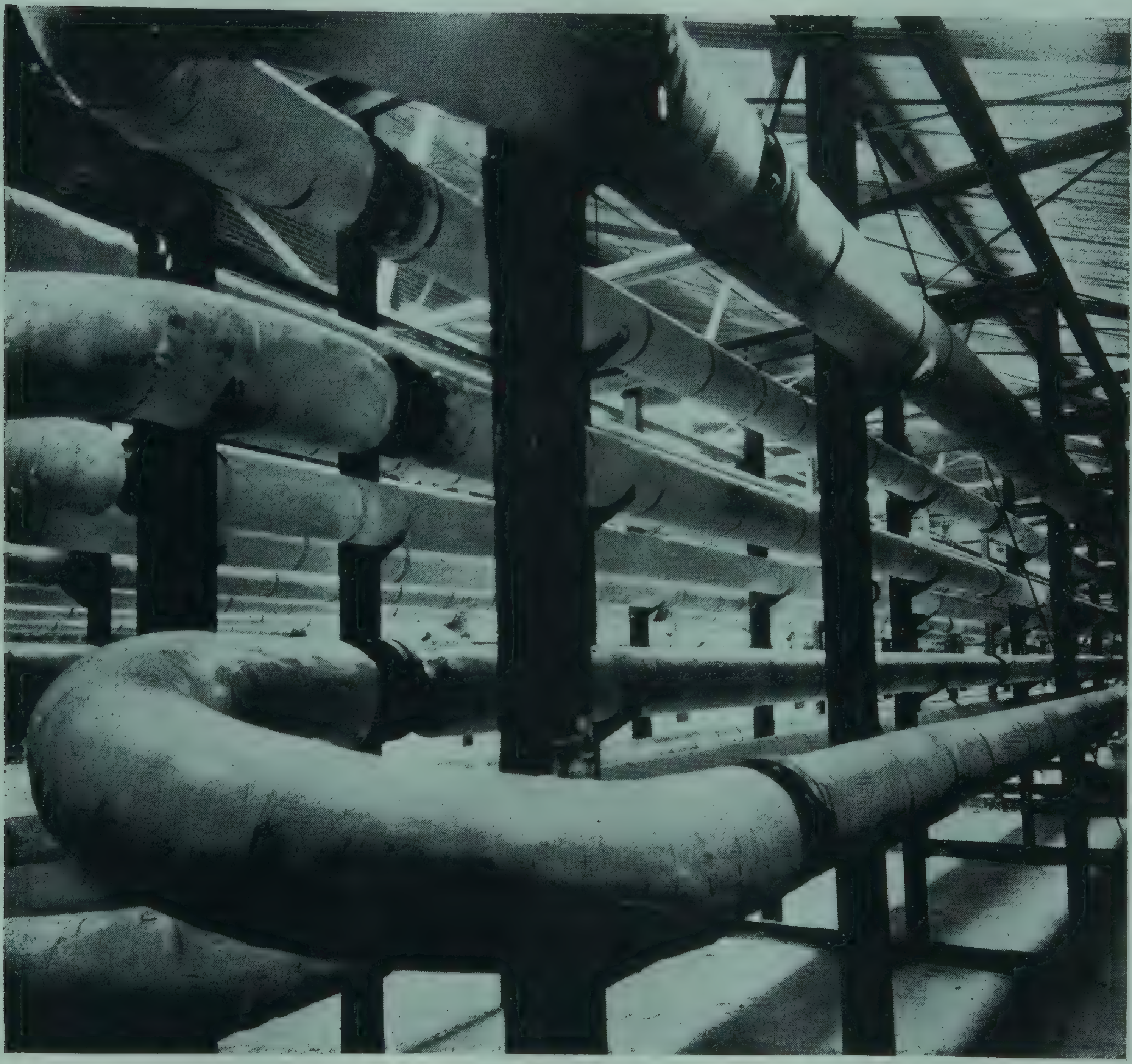

Fig. 12. Continuous digester for nitrocellulose viscosity reduction (Milliken[192]).

According to Brissaud,[205] the ease of dehydration is affected primarily by solubility and swelling in the alcohol; these properties, in turn, are a function of the nitrogen content and uniformity of nitration.

(c) REACTIONS OF NITROCELLULOSE

Although nitrocellulose is an ester, treatment of it with the usual saponification agents (aqueous alkalies) does not yield cellulose and the corresponding alkali nitrate. Instead, marked decomposition takes place with the formation of the alkali nitrite and decomposition products of cellulose. The products reported by various investigators as having been formed by the action of alkalies on nitrocellulose include inorganic nitrates and nitrites;[206,207] ammonia;[207] cyanide;[208] carbon dioxide;[209] oxalic acid;[206,210,211] malic, glycolic, trihydroxyglutaric, dihydroxybutyric, malonic, and tartronic acids;[210] sugars;[207,212] modified celluloses[207] and their nitrates;[213] partially denitrated nitrocelluloses;[212,214,215] and a product which is believed to be either hydroxypyruvic acid[216] ($CH_2OH{\cdot}CO{\cdot}COOH$) or 2-hydroxy-3-oxopropionic acid[217] ($CHO{\cdot}CHOH{\cdot}COOH$). Quantitative measurements have been made of the formation of nitrites[218] and of the decomposition of nitrocellulose[219,220] as shown by alkali consumption. The most extensive quantitative investigation of the alkaline decomposition of nitrocellulose has been carried out by Kenyon and Gray,[221] who found that relatively small amounts of CO_2 are produced and relatively large proportions of the nitrate groups are reduced to nitrite. The production of CO_2 and reducing substances appears to be related to time, concentration of alkali, ratio of alkali to nitrocellulose, and temperature.

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[205] L. Brissaud, *Mém. poudres*, **31**, 145 (1949).

[206] E. Hadow, *J. Chem. Soc.*, **7**, 201 (1855).

[207] A. Béchamp, *Compt. rend.*, **41**, 817 (1855).

[208] W. Will, *Ber.*, **24**, 400 (1891).

[209] H. Vohl, *Dinglers Polytech. J.*, **112**, 236 (1849).

[210] E. Berl and A. Fodor, *Z. ges. Schiess- u. Sprengstoffw.*, **5**, 296 (1910).

[211] W. G. Mixter, *Am. Chem. J.*, **13**, 507 (1891).

[212] A. Béchamp, *Bull. soc. chim.*, [1], **3**, 289 (1863).

[213] E. Berl and A. Fodor, *Z. ges. Schiess- u. Sprengstoffw.*, **5**, 254 (1910).

[214] A. Béchamp, *Ann. chim. phys.*, [3], **46**, 338 (1856).

[215] J. M. Eder, *Ber.*, **13**, 169 (1880).

[216] J. H. Aberson, *Z. physik. Chem.*, **31**, 17 (1899).

[217] C. Neuberg and M. Silbermann, *Z. physiol. Chem.*, **44**, 134 (1905).

[218] L. Vignon and I. Bay, *Compt. rend.*, **135**, 507 (1902); T. Carlson, *Arkiv. Kemi Mineral. Geol.*, **3**, Art. 8, 1–15; *Ber.*, **40**, 4191 (1907).

[219] O. Silberrad and R. C. Farmer, *J. Chem. Soc.*, **89**, 1759 (1906).

[220] C. Piest, *Z. angew. Chem.*, **23**, 1009 (1910).

[221] W. O. Kenyon and H. LeB. Gray, *J. Am. Chem. Soc.*, **58**, 1422 (1936); this reference contains a good review of the literature on the alkaline decomposition of nitrocellulose.

In attempting to explain the mechanism of alkaline decomposition of nitric acid esters, Berthelot[222] suggested that it may take place in the following way:

$$RCH_2ONO_2 + NaOH \rightarrow RCHO + NaNO_2 + H_2O \qquad (2)$$

Klason and Carlson[223] elaborated on this hypothesis and suggested that the primary products are a peroxide and a nitrite:

$$RCH_2ONO_2 + NaOH \rightarrow RCH_2OOH + NaNO_2 \qquad (3)$$

In the ordinary course of events, the peroxide will decompose into an aldehyde and water:

$$RCH_2OOH \rightarrow RCHO + H_2O \qquad (4)$$

but when a reducing agent is present, the peroxide is reduced to the alcohol.

The assumption that simultaneous oxidation and reduction take place in the treatment of nitrocellulose (and other nitric acid esters, such as nitroglycerin) with alkali, makes it easy to account for many of the products actually obtained.[224] However, Farmer[225] favors the view of Berl and Delpy[226] that the initial reaction is hydrolysis and suggests that nitric acid and alcohol may be formed momentarily and that the alcohol is immediately oxidized by the nitric acid. Lucas and Hammett[227] studied the formation of benzaldehyde and sodium nitrite from benzyl nitrate in the presence of NaOH. They felt that evidence was insufficient to suggest a mechanism for this oxidation-reduction reaction. (See Section G of this Chapter IX.)

The ability to saponify nitrocellulose to cellulose with alkalies in the presence of reducing agents has been applied commercially in the manufacture of sausage casings and rayon by the "nitrocellulose" process. In this process, the nitrocellulose fibers and casings are denitrated by treatment with alkaline hydrosulfides. Reichel and Craver[228] recommended carrying out the denitration on swollen nitrocellulose with a solution containing not over 5% of an alkali hydrosulfide at a temperature not exceeding 20°C.

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[222] M. Berthelot, *Compt. rend.*, **131**, 519 (1900).

[223] P. Klason and T. Carlson, *Ber.*, **39**, 2752 (1906).

[224] T. M. Lowry, K. C. Browning, and J. W. Farmery, *J. Chem. Soc.*, **117**, 552 (1920)

[225] R. C. Farmer, *J. Chem. Soc.*, **117**, 806 (1920).

[226] E. Berl and M. Delpy, *Ber.*, **43**, 1421 (1910).

[227] G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, **64**, 1928 (1942).

[228] F. H. Reichel and A. E. Craver (to Sylvania Industrial Corp.), U. S. Patent 2,289,-520 (July 14, 1942); *Chem. Abstracts*, **37**, 532 (1943).

Reichel and Cornwell[229] proposed that denitration of sausage tubings and filaments containing nitrocellulose should be carried out with an alkaline solution of an alkali hydrosulfide maintained at a pH below 12 by addition of a buffer consisting of the salt of a strong acid and a weak base.

Denitration of nitrocellulose also takes place on treatment with acids, but the reaction is much slower than when alkalies are used.[225] Acid denitration has been exemplified in the treatment of nitrocellulose with mixed acid containing more water than the acid used to produce this nitrocellulose; in this case, the esterification equilibrium shifts in the direction of lower nitrogen content. One practical aspect of this behavior is observed in the denitration of nitrocellulose which occurs while wringing out the spent acid. This denitration is caused by dilution of the spent acid with moisture from humid air; the superficial denitration which occurs decreases the solubility of the product.[230,231] Desmaroux[232] observed that the effectiveness of denitration of nitrocellulose with dilute solutions of HNO_3, HCl, and H_2SO_4 decreases in the order named and concluded that the denitrating action decreases with increase in size of the acid anion.

Thinius[233] denitrated water-wet nitrocellulose suspended in an inert organic liquid, such as carbon tetrachloride, by treatment with an inorganic acid chloride, such as PCl_3, $POCl_3$, or $SOCl_2$. Using this method, he obtained from nitrocellulose with 13.4% N a product with good solubility and a 12.7% N content.

Treatment of nitrocellulose with lithium aluminum hydride causes complete denitration which is accompanied by extensive depolymerization.[234] Simultaneous denitration and acetylation result when nitrocellulose dissolved in acetic anhydride is treated with zinc dust and anhydrous hydrogen chloride.[235] The resulting cellulose acetate has a much lower D.P. than the original nitrocellulose.

Treatment of nitrocellulose (11.7% N) with a solution of sodium, sodamide, or potassium amide in liquid ammonia yielded a product with

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[229] F. H. Reichel and R. T. K. Cornwell (to American Viscose Corp.), U. S. Patent 2,421,391 (June 3, 1947); *Chem. Abstracts*, **41**, 5306 (1947).

[230] I. M. Naiman, N. D. Troitzkaya, and Ya. G. Danyushevskii, *Rev. gén. mat. plastiques*, **11**, 273, 303, 333 (1935).

[231] K. Fabel, *Nitrocellulose*, **12**, 143 (1941).

[232] J. Desmaroux, *Compt. rend.*, **206**, 1483 (1938).

[233] K. Thinius (to Deutsche Celluloid-Fabrik Akt.-Ges.), German Patent 723,628 (Aug. 7, 1942); *Chem. Abstracts*, **37**, 5590 (1943).

[234] L. M. Soffer, E. W. Parrotta, and J. DiDomenico, *J. Am. Chem. Soc.*, **74**, 5301 (1952).

[235] D. O. Hoffman, R. S. Bower, and M. L. Wolfrom, *J. Am. Chem. Soc.*, **69**, 249 (1947).

8.1% N which was claimed by the authors to be a cellulose amine.[236] When the treatment was carried out with sodium acetylide in liquid ammonia, an aminocellulose acetylide was obtained.[237] In the light of present-day knowledge, it is likely that products such as the above were so highly degraded that they could hardly be called cellulose compounds.

Segall and Purves[238] investigated the reaction of nitrocellulose (13.9% N; D.S. 2.92) with hydroxylamine, *O*-methoxyamine, and their hydrochlorides in dry pyridine. In all four cases, the nitrate substitution was reduced to about 1.7. The degree of substitution of oxime groups in the product was as follows: hydroxylamine—0.08, *O*-methoxyamine—0.02, hydroxylamine hydrochloride—1, *O*-methoxyamine hydrochloride—1.

(d) CONSTITUTION OF NITROCELLULOSE

Since the constitution of cellulose and its derivatives is discussed in Chapter III, reference will be made here only to some findings which deal specifically with nitrocellulose.

The degree of polymerization (that is, the number of anhydroglucose units in the molecule or D.P.), determined viscometrically, of a number of nitrocelluloses was found by Staudinger and Sohn[239] to be appreciably higher than that of the original celluloses calculated from viscosity measurements in cuprammonium hydroxide solution. On the other hand, when the celluloses were dissolved in cuprammonium hydroxide solution, recovered by precipitation, and then nitrated, the D.P. of the nitrocelluloses was the same as that of the original celluloses. According to Staudinger and Sohn, this behavior may be explained by the assumption that (a) ester linkages are formed in the cellulose chain by oxidation (particularly with acidic agents) which are stable in the nitrating acid but are readily hydrolyzed by alkali, or (b) end groups of a broken chain molecule in the cellulose fiber are condensed and linked together by the dehydrating action of the nitrating acid.

Although there is no evidence showing the existence of the ester linkages proposed by Staudinger and Sohn, there is evidence favoring the view that the viscosity behavior discussed above is due to the presence of alkali-sensitive groups in the cellulose rather than to a condensation reaction taking place during nitration. Thus, in an investigation of the oxidation of cellulose, Davidson[240] found that oxycellulose produced by neutral or acid oxidation suffered a loss in nitrocellulose viscosity (that is, the viscosity of a solution of nitrocellulose prepared from a given cellulose) on treatment with alkali. He suggested that certain types of oxidation do not result in direct scission of the cellulose chain molecule but produce alkali-sensitive groupings in the molecule.

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[236] P. C. Scherer and J. M. Feild, *Rayon Textile Monthly*, **22**, 607 (1941).

[237] P. C. Scherer and J. M. Saul, *Rayon Textile Monthly*, **28**, 474, 537 (1947).

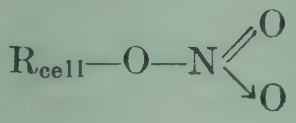
[238] G. H. Segall and C. B. Purves, *Can. J. Chem.*, **30**, 860 (1952).

[239] H. Staudinger and A. W. Sohn, *Naturwissenschaften*, **27**, 548 (1939); *Ber.*, **72B**, 1709 (1939); *J. prakt. Chem.*, **155**, 177 (1940); *Melliand Textilber.*, **21**, 205 (1940); *Cellulosechemie*, **18**, 25 (1940).

An attempt[241] has been made to determine the distribution of nitrate groups in partially nitrated cellulose based on the knowledge that sodium iodide replaces primary nitrate groups with iodine in simple sugar nitrates. The method was unsuitable for highly nitrated nitrocellulose (13.2% N) because of oxidative side reactions. On treatment of other nitrocelluloses (2.5–9.0% N) with sodium iodide, about one-half of the nitrate groups were replaced by iodine, about one-third remained unchanged, and the rest were removed. The results are taken to indicate that at least one-half of the nitrate groups in the low-substitution nitrocelluloses are in the primary position.

Wide variations have been noted in the electrochemical activity of membranes prepared from nitrocellulose solutions (collodion). The electrochemical activity is believed to be due to the presence in the nitrocellulose molecules of carboxyl groups which are formed as the result of oxidation.[242]

Champetier and Clément[243] measured the infrared absorption spectrum of nitrocellulose with the object of determining the structure of the ester group. Their results led them to propose that the nitrate group in nitrocellulose has the following structure:



$$\mathrm{R_{cell}{-}O{-}N}\begin{smallmatrix} =\mathrm{O} \\ \rightarrow\mathrm{O} \end{smallmatrix}$$

2. Cellulose Sulfate

The ability of concentrated sulfuric acid (preferably about 72% strength) to dissolve cellulose has been known for over a century. If the cellulose is precipitated immediately after dissolving, it contains little or no combined sulfate. Esterification will take place if the cellulose is left in solution for a

[240] G. F. Davidson, *J. Textile Inst.*, **29,** T195 (1938); **31,** T81 (1940).

[241] G. E. Murray and C. B. Purves, *J. Am. Chem. Soc.*, **62,** 3194 (1940).

[242] K. Sollner, I. Abrams, and C. W. Carr, *J. Gen. Physiol.*, **24,** 467 (1941); **25,** 7 (1941).

[243] G Champetier and P. L. Clément, *Compt. rend.*, **224,** 199 (1946).

time. Reference has already been made to the formation of mixed sulfuric–nitric acid esters of cellulose during nitration with H_2SO_4–HNO_3 mixtures.

A great many methods for preparing cellulose sulfate and its salts have been reported, as will be evident from the discussion which follows. However, the processes[244,245] which have most closely approached commercial success are based on the use of a mixture of sulfuric acid and isopropyl alcohol as the sulfating agent. In the process described by Frank[244] fibrous water-soluble cellulose sulfate is prepared by treating cellulose with sulfuric acid and a suitable amount of an aliphatic alcohol. Malm and Crane[245] also developed a fibrous process for making cellulose sulfate in which they treated cellulose with sulfuric acid in presence of an aliphatic alcohol, ammonium sulfate, and an inert diluent such as kerosene, benzene, or toluene.

A high-quality sodium cellulose sulfate, with a degree of substitution (D.S.) of about 1, was introduced commercially in 1950[246] but was subsequently withdrawn from the market. This product is soluble in hot or cold water and yields clear, highly viscous, neutral aqueous solutions at relatively low concentrations. Sodium cellulose sulfate has been recommended for use as a thickening agent in water and emulsion paints, food products, and textile printing pastes; as a sizing and finishing agent for textile fibers; and as a greaseproof and oilproof coating and a sizing agent for paper.

Braconnot[247] reported in 1819 that linen dissolves in cold concentrated sulfuric acid and that on dilution with water a clear solution is obtained which contains, in addition to H_2SO_4, another acid which he called "acide végéto sulphurique." The barium salt of this acid, which remained in solution, could be precipitated by addition of alcohol. Analysis of the salt by de Carolles[248] showed that the amount of Ba combined with the cellulose increased with time of contact between the concentrated H_2SO_4 and the cellulose; the product obtained after the solution was allowed to stand for 24 hrs. before dilution was reported to have a composition corresponding to $C_4H_8O_4(SO_3)_2BaO \cdot 2H_2O$. A barium salt[249] with the composition

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[244] G. Frank, U. S. Patent 2,559,914 (July 10, 1951); *Chem. Abstracts*, **45**, 8770 (1951).

[245] C. J. Malm and C. L. Crane (to Eastman Kodak Co.), U. S. Patent 2,539,451 (Jan. 30, 1951); *Chem. Abstracts*, **45**, 4453 (1951).

[246] Tennessee Eastman Corp., *Sodium Cellulose Sulfate*, Tennessee Eastman Corp., Kingsport, Tenn., 1950, 4 pp.

[247] H. Braconnot, *Ann. chim. phys.*, [2], **12**, 185 (1819).

[248] B. de Carolles, *Ann.*, **52**, 412 (1844).

[249] H. Fehling, *Ann.*, **53**, 135 (1845).

$C_{90}H_{180}O_{90}BaO(SO_3)_2$ and a lime salt[250] corresponding to $C_{33}H_{28}O_8(SO_3)_2CaO$ have also been reported.

Hönig and Schubert[251] dissolved cellulose in concentrated H_2SO_4 at room temperature and prepared Cu, Pb, and Ba salts of the cellulose sulfate. They confirmed de Carolles' observation that the ratio of Ba to H_2SO_4 in the salts is always 1:2. Stern[252] neutralized a sulfuric acid solution of cellulose with baryta and decanted the clear liquid after $BaSO_4$ had settled out. He concentrated the clear liquid on a water bath and then under vacuum; the solution remained neutral. The Ba salt was precipitated by adding alcohol, and after purification and drying, was obtained in 48% yield as a white hygroscopic powder with a composition corresponding to $C_6H_8O_3(SO_4)_2Ba$. Kagawa[253] reported that a better product (sodium cellulose sulfate) is obtained by neutralizing the sulfuric acid solution of cellulose with Na_2CO_3 and removing the sodium sulfate by dialysis. Champetier and Bonnet[254] found that aqueous solutions containing up to 54% H_2SO_4 yield H_2SO_4 addition compounds with cellulose which are decomposed on washing with water. Higher concentrations of H_2SO_4 yield cellulose sulfate; with 64% H_2SO_4 a cellulose sulfate corresponding to $C_6H_9O_5 \cdot SO_3H$ is obtained.

Traube,[255] Blaser, and Grunert[256] found that well-dried cellulose combines with SO_3 vapors without charring to form cellulose trisulfate; the formation of lower sulfates could not be detected. When sufficient SO_3 had been added for complete esterification, the product was dissolved in water and treated with a slight excess of $PbCO_3$. After removal of the Pb with H_2S, the product was neutralized with KOH. On cooling the solution, separation of "potassium cellulose trisulfate A" occurred; this product, which was obtained in 65% yield had a composition corresponding to $C_6H_7O_2(SO_4K)_3$. Concentration of the mother liquor yielded more material of the same composition but with different specific rotation.

Gebauer-Fülnegg,[257] Stevens, and Dingler[258] esterified cellulose with a mixture of chlorosulfonic acid ($ClSO_3H$) and pyridine at 100°C. until complete solution occurred. On addition of alcohol, the pyridine salt of cellulose sulfate was precipitated; with alcohol containing NaOH or NaCl, the sodium salt was obtained. Addition of Ba salts to solutions of the other salts yielded a Ba salt of the cellulose sulfate which was insoluble in water and very resistant to acid hydrolysis. Analysis showed that the products prepared by this process were almost completely esterified; that is, the D.S. was nearly 3.0. In order to determine the extent of degradation that had occurred in the esterification, they investigated methods for removing the sulfate without excessive decomposition. This was finally accomplished by treating the cellulose sulfate with methanol containing 0.5% HCl for 6 hrs. under reflux. The regenerated, sulfur-free cellulose showed a specific rotation in cuprammonium hydroxide solution similar to that of native cellulose. It could also be converted to trimethyl cellulose and cellulose triacetate.[259] However, no data indicative of molecular weight were presented to prove that the product had not been strongly degraded.

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[250] R. Marchand, *J. prakt. Chem.*, **35**, 199 (1845).

[251] M. Hönig and S. Schubert, *Monatsh.*, **6**, 708 (1885).

[252] A. L. Stern, *J. Chem. Soc.*, **67**, 74 (1895).

[253] I. Kagawa, *J. Soc. Textile and Cellulose Ind., Japan*, **1**, 681 (1945); through *Che*... *Abstracts*, **44**, 7533 (1950).

[254] G. Champetier and J. Bonnet, *Bull. soc. chim.*, [5], **10**, 585 (1943).

[255] W. Traube, French Patent 657,204 (Jan. 11, 1929).

[256] W. Traube, B. Blaser, and C. Grunert, *Ber.*, **61B**, 754 (1928).

[257] E. Gebauer-Fülnegg (to E. I. du Pont de Nemours & Co.), U. S. Patent 1,734,291 (Nov. 5, 1929); *Chem. Abstracts*, **24**, 498 (1930).

[258] E. Gebauer-Fülnegg, W. H. Stevens, and O. Dingler, *Ber.*, **61B**, 2000 (1928).

Traube and coworkers[260] studied the $ClSO_3H$–pyridine esterification process and found that the product ordinarily obtained had a D.S. of about 2.6; prolonged esterification yielded a product with D.S. 2.9. A comparative study of the SO_3 process showed that it is advantageous to use a carbon disulfide solution of SO_3 in place of gaseous SO_3 and to have an excess of cellulose present. The reaction mixture is worked up by pouring it into an excess of KOH solution, filtering off the unesterified cellulose, and recovering the potassium cellulose trisulfate as before. The viscosity of a 1% aqueous solution of sodium cellulose sulfate (D.S. 2.6) prepared by the $ClSO_3H$–pyridine method was found to be much higher than that of a similar solution of potassium cellulose trisulfate prepared by the SO_3 process. This was taken to indicate that appreciable depolymerization had taken place in the latter case. Hagedorn and Guehring[261] have claimed the preparation of cellulose sulfate by reacting alkali cellulose with an oxygen-containing chloride of sulfuric acid (for example, SO_2Cl_2) in the presence of benzene. Haskins[262] prepared a cellulose ester containing substantially only sulfate groups by treating cellulose with a mixture of sulfuric acid, pyridine, and an organic acid anhydride in which there is not a molar excess of anhydride over sulfuric acid in the form of its pyridine salt. Schulze[263] prepared cellulose sulfate by treatment of cellulose with SO_3 in the presence of a tertiary amine such as pyridine. Rigby esterified cellulose with (a) pyrosulfuric acid ($H_2S_2O_7$) or its equivalent in the presence of a tertiary amine like pyridine,[264] and (b) a mixture of a substance containing the radical $-\text{O}-\overset{|}{\text{S}}\text{O}_2$ (for example, chlorosulfonic acid), a tertiary amine, and an inert diluent (for example, toluene).[265] Rubenstein[266] prepared cellulose sulfate insoluble in water but soluble in cold dilute NaOH solution by treating cellulose with up to 0.5 mole of a sulfating agent in presence of NaOH or a tertiary cyclic amine.

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[259] E. Gebauer-Fülnegg and O. Dingler, *J. Am. Chem. Soc.*, **52**, 2849 (1930).

[260] W. Traube, B. Blaser, and E. Lindemann, *Ber.*, **65B**, 603 (1932).

[261] M. Hagedorn and E. Guehring (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,848,524 (Mar. 8, 1932).

[262] J. F. Haskins (to Du Pont Rayon Co.), U. S. Patent 1,866,532 (July 12, 1932).

Crane[267] obtained stable, water-soluble cellulose acetate sulfates, in the form of salts of sodium or other metals, by treating cellulose with relatively large quantities of H_2SO_4 in presence of acetic acid and acetic anhydride and neutralizing the mixed esters with a metal salt. One of the products contained 20.7% sulfur and 1.8% acetyl. Crane[268] also prepared cellulose acetate sulfates with high sulfur content by treating cellulose with acetic acid, acetic anhydride, and sulfuric acid in the presence of a substantial amount of a bisulfate which prevents the product from dissolving in the reaction mixture. Araki[269] prepared a mixed cellulose ester (for example, cellulose acetate sulfate) and treated it with alkali to remove selectively the organic acid groups and leave a pure cellulose sulfate.

Thomas[270] obtained cellulose sulfate with D.S. less than 0.5 by heating cellulose impregnated with an aqueous solution of sulfamic acid ($H_2N \cdot SO_2 \cdot OH$) and urea. The ammonium cellulose sulfate was insoluble in water but soluble in 10% NaOH solution at −10°C.

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[263] F. Schulze (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,016,299 (Oct. 8, 1935).

[264] G. W. Rigby (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,025,073 (Dec. 24, 1935).

[265] G. W. Rigby (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,033,787 (Mar. 10, 1936).

[266] L. Rubenstein (to Imperial Chemical Industries Ltd.), U. S. Patent 2,042,484 (June 2, 1936); *Chem. Abstracts*, **30**, 5037 (1936).

[267] C. L. Crane (to Eastman Kodak Co.), U. S. Patent 2,582,009 (Jan. 8, 1952); *Chem. Abstracts*, **46**, 3275 (1952).

[268] C. L. Crane (to Eastman Kodak Co.), U. S. Patent 2,622,079 (Dec. 16, 1952); *Chem. Abstracts*, **47**, 3565 (1953).

[269] T. Araki (to Tokyo Industrial Research Inst.), Japanese Patent 176,243 (May 18, 1948); *Chem. Abstracts*, **45**, 5406 (1951).

[270] J. C. Thomas (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,511,229 (June 13, 1950); *Chem. Abstracts*, **44**, 8657 (1950).

Jullander[271] prepared cellulose sulfate by treating cellulose with H_2SO_4 (in admixture with a lower alcohol) in the presence of an immiscible diluent (toluene or ethylene dichloride) and a small amount of a saturated or unsaturated fatty acid as an emulsifying agent.

A water-soluble ammonium cellulose sulfate containing not less than 25% combined H_2SO_4 was obtained by Ward and Tallis[272] by heating cellulose impregnated with an aqueous solution containing H_2SO_4, cyanamide, and ammonium sulfate or an alkali metal sulfate. The product from this process could be made insoluble in water and solutions of alkali by impregnating it with an aqueous alcoholic solution of the salt of a polyvalent metal ($CaCl_2$, $AlCl_3$, $ZnCl_2$) and drying the impregnated material.[273]

Caille[274] treated strips of cotton cloth with a mixture of equal parts of H_2SO_4 and acetic acid at 45°C. for 30 min. The product, which retained its original fibrous structure, could be washed neutral with alcohol or calcareous water; washing with ordinary water caused hydrolysis. Heat tests showed that the stability of the product increases with increasing neutralization of the combined acid groups by the alkaline constituents of the wash water. The cotton cloth had an affinity for basic dyes. Numerous patents have been granted covering superficial treatments of cellulose with compounds of sulfur to change its dyeing properties and its resistance to water.[275]

3. Cellulose Phosphate

Champetier[276] has reported the formation of an addition compound having the composition $3C_6H_{10}O_5 \cdot H_3PO_4$ on treatment of cellulose with aqueous phosphoric acid solutions. The addition compound was destroyed by washing with water; the fibrous cellulose was recovered apparently unchanged. Cellulose phosphate (containing about 16% PO_4) has been prepared by treating cellulose with an oxygen-containing chloride of phosphoric acid in the presence of benzene.[261] Tanner[277] prepared a product containing about 17% phosphorus (cellulose triphosphate would have 23% P) by treating cellulose with a mixture containing concentrated sulfuric and phosphoric acids and a small amount of a weak acid catalyst (for example, glacial acetic, boric, or formic acid). Cellulose phosphate may be prepared by treating cellulose with moderately concentrated phosphoric acid and $POCl_3$ with or without the addition of a diluent.[278] In a modification of this process, cellulose is treated with concentrated phosphoric acid and a small amount of another inorganic acid (for example, H_2SO_4); the cellulose ester is precipitated by addition of water to the reaction mixture.[279]

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[271] I. Jullander (to Mo och Domsjo Aktiebolag), Swedish Patent 137,018 (Aug. 26, 1952); *Chem. Abstracts*, **47**, 4607 (1953).

[272] F. Ward and E. E. Tallis (to Courtaulds Ltd.), U. S. Patent 2,603,551 (July 15, 1952); *Chem. Abstracts*, **46**, 8371 (1952).

[273] F. Ward (to Courtaulds Ltd. and F. Ward), Brit. Patent 670,346 (Apr. 16, 1952); *Chem. Abstracts*, **46**, 8371 (1952).

[274] A. Caille, *Chimie & industrie*, **15**, 189 (1926).

[275] O. Faust, *Celluloseverbindungen und besonders wichtige Verwendungsgebiete*, J Springer, Berlin, 1935, p. 518.

[276] G. Champetier, *Compt. rend.*, **196**, 930 (1933); *Ann. chim.*, [10], **20**, 5 (1933).

Malm and Fordyce[280] prepared an insoluble phosphorus compound by treating cellulose with an acid chloride of a phosphoric acid ester in which one chlorine atom is attached to the phosphorus atom of each molecule, for example, dicresyl chlorophosphate. Cellulose phosphodiamide was obtained by treating cellulose with phosphoryl chloride and then treating the product with ammonia.[281] Daul and Reid[282] prepared the pentaerythritol phosphoric acid ester of cellulose by heating cellulose impregnated with pentaerythritol phosphoric acid. By similar treatment with polyvinyl phosphoric acid, they obtained the corresponding cellulose ester.[283]

Much of the work on the preparation of cellulose phosphates has been done with the object of developing a treatment for flameproofing textiles made from cellulose fibers. In a comprehensive study of this subject, Coppick and Hall[284] reported that treatment of cellulose at 150° to 200°C. with phosphoric acid and urea yielded a cellulose phosphate without causing excessive damage to the fibers. Reid and Mazzeno[285] obtained products containing phosphorus and chlorine by treating cotton cloth with $POCl_3$ and pyridine. Patents have also been issued covering the modification of the dyeing and other properties of cellulose by superficial treatment with a variety of phosphorus compounds.[275]

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[277] W. L. Tanner (to National Chemical and Mfg. Co.), U. S. Patent 1,896,725 (Feb. 7, 1933).

[278] I. G. Farbenindustrie Akt.-Ges., German Patent 547,812 (Mar. 29, 1932).

[279] I. G. Farbenindustrie Akt.-Ges., German Patent 556,590 (Aug. 17, 1932); *Chem. Abstracts*, **27**, 413 (1933).

[280] C. J. Malm and C. R. Fordyce (to Eastman Kodak Co.), U. S. Patent 2,008,986 (July 23, 1935); *Chem. Abstracts*, **29**, 6055 (1935).

[281] C. A. Thomas and G. Kosolapoff (to Monsanto Chemical Co.), U. S. Patent 2,401,440 (June 4, 1946); *Chem. Abstracts*, **40**, 5250 (1946).

[282] G. C. Daul and J. D. Reid (to the U. S. Secretary of Agriculture), U. S. Patent 2,592,544 (April 15, 1952); *Chem. Abstracts*, **46**, 7768 (1952).

[283] G. C. Daul and J. D. Reid (to the U. S. Secretary of Agriculture), U. S. Patent 2,610,953 (Sept. 16, 1952); *Chem. Abstracts*, **47**, 1389 (1953).

[284] S. Coppick and W. P. Hall, in R. W. Little, editor, *Flameproofing Textile Fabrics*, Reinhold, New York, 1947, p. 179; see also A. C. Nuessle, *J. Soc. Dyers Colourists*, **64**, 342 (1948).

4. Cellulose Esters of Other Inorganic Acids

Treatment of cotton with thionyl chloride ($SOCl_2$) in presence of pyridine resulted in the introduction of one atom of chlorine for each $C_6H_{10}O_5$ group; the reaction product was dark in color and almost a powder.[286] An attempt has been made to esterify cellulose by dissolving it in fluorosulfonic acid (FSO_3H), but results on identification of the cellulose ester formed are inconclusive.[287] Sulfur was introduced into cellulose by treating hydrocellulose with sulfur monochloride in hydrochloric acid.[288] It will be noted that in none of the above cases was a high polymer derivative obtained with certainty.

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[285] J. D. Reid and L. W. Mazzeno, Jr., *Ind. Eng. Chem.*, **41**, 2828 (1949); see also J. D. Reid, L. W. Mazzeno, Jr., and E. M. Buras, Jr., *Ind. Eng. Chem.*, **41**, 2831 (1949).

[286] P. Carré and P. Mauclère, *Compt. rend.*, **192**, 1567 (1931).

[287] C. H. Möllering, *J. prakt. Chem.*, **134**, 209 (1932).

[288] R. Sthamer, German Patent 137,206 (Dec. 2, 1902)

C. ORGANIC ESTERS

CARL J. MALM AND GORDON D. HIATT

Cellulose as a polyhydroxy alcohol offers the possibility of ester formation with any organic acid. The complexity of the cellulose molecule, however, makes it difficult to obtain a high degree of esterification with many acids, and also limits the variety of reaction methods which can be successfully applied. Esters of a high degree of esterification have, therefore, been confined largely to the normal fatty acid series and to the simpler aromatic acids.

Derivatives of cellulose are usually prepared with the objective of obtaining physical properties not possessed by cellulose itself. Treatments which result in only slightly modified cellulose, yielding no soluble derivatives or no greatly changed physical properties, are therefore of comparatively minor interest. It is also important that the derivative be produced under conditions which do not excessively degrade the cellulose.

Methods for preparation of cellulose esters may in general be classified as esterification by reaction of (a) acids, (b) anhydrides, and (c) acid chlorides.

Appreciable esterification by direct treatment of cellulose with an organic acid is possible only in the case of the formate.[1] Room temperature treatment of cellulose with formic acid results in introduction of a small amount of formyl; by addition of a catalyst this may be increased to a sufficiently high degree of esterification to produce soluble products.

At room temperature other organic acids react only to a very slight degree with cellulose. Clarke and Malm[2] have shown that acetic, propionic, and butyric acids at their boiling points produce minor degrees of esterification, the exact extent depending upon the reactivity of the cellulose. Treatment with higher acids results in only low degrees of reaction. The use of catalysts to promote reaction usually results in severe degradation and has not been a useful esterification procedure.

Acids can be made to react with cellulose by using substituted anhydrides, which in themselves do not esterify cellulose, as impelling agents to bring about reaction. This process has been found to have wide applicability and may be used as a general method of esterification, particularly with high molecular weight acids. As impelling agents, anhydrides of halogen-substituted[3–5] or alkoxy-substituted[6] acetic acid are effective, monochloroacetic anhydride being the most useful material for general application. A reaction mixture of 1 part of cellulose with 5 parts of chloroacetic anhydride, 0.01 part of magnesium perchlorate as catalyst, and slightly more than the calculated amount of the acid to be esterified may be reacted at 60–70°C., resulting in a solution of the cellulose ester within a few hours.

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[1] I. Sakurada, *J. Soc. Chem. Ind., Japan,* **35,** B123 (1932).

[2] H. T. Clarke and C. J. Malm, *J. Am. Chem. Soc.,* **51,** 274 (1929).

The impelling agent in this process brings about conversion of the esterification acid to its anhydride. The reaction is thus an esterification by anhydride, but it is only necessary to use a slight excess of the calculated amount of acyl to react with the cellulose, whereas usual anhydride reactions require at least double that amount. High molecular weight acids are poor solvents for their reaction product, are difficult to wash out, and are, therefore, undesirable components of a reaction mixture.

Esterification by acid anhydrides in the presence of mineral acid catalysts is the most widely known process of esterification because of its commercial use for cellulose acetate manufacture. The same general process may be made to operate with propionic and butyric anhydrides, but for aromatic anhydrides or aliphatic anhydrides of higher molecular weight the reactivity is not sufficient to produce high degrees of esterification. Soluble cellulose derivatives containing free hydroxyl groups, such as acetone-soluble cellulose acetate, may, however, be treated with higher anhydrides in the presence of acid catalysts to esterify the free hydroxyl groups and yield mixed esters.

Ketene has been suggested as an acetylation reagent.[7,8] It does not react directly with cellulose but through formation of acetic anhydride. Con-

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[3] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patent 1,880,808 (Oct. 4, 1932); *Chem. Abstracts*, **27**, 600 (1933); Brit. Patent 313,408 (Aug. 27, 1929); *Chem. Abstracts*, **24**, 1217 (1930).

[4] A. Gundlach and T. Becker (to I.G. Farbenindustrie Akt.-Ges.), German Patent 516,250 (Jan. 20, 1931); *Chem. Abstracts*, **25**, 1993 (1931).

[5] M. Stacey, E. J. Bourne, J. C. Tatlow, and J. M. Tedder, *Nature*, **164**, 705 (1949).

[6] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patent 1,987,053 (Jan. 8, 1935); *Chem. Abstracts*, **29**, 1634 (1935).

[7] D. A. Nightingale (to Ketoid Co.), U. S. Patent 1,604,471 (Oct. 12, 1926); *Chem. Abstracts*, **21**, 176 (1927).

[8] G. D. Graves (to E. I. du Pont de Nemours & Co.), U. S. Patent, 1,990,483 (Feb. 12, 1935); *Chem. Abstracts*, **29**, 1983 (1935).

siderable color accompanies its use. It is more desirable to prepare and purify the anhydride as a separate operation.

Tertiary organic bases, such as pyridine, may be used as reaction media for organic anhydrides, but even at reflux temperatures the activity is not sufficient to produce complete esterification, except for special cases, such as the action of acetic anhydride on exceptionally reactive forms of cellulose. This type of reaction is, therefore, generally useful only for partial esterification. Use of pyridine hydrochloride as a reaction medium for anhydrides provides a much stronger reaction condition.[9] The greater activity may be explained by formation of acid chlorides as the effective esterification agents.

Acid chlorides of nearly all types of organic acids may be depended upon to react with cellulose in the presence of pyridine as a reaction medium. The reaction is carried out at elevated temperatures, usually at 100°C. In certain cases, such as with acetyl chloride and toluenesulfonyl chloride, secondary reactions result in the introduction of appreciable quantities of combined nitrogen and chlorine into the cellulose derivative, making special precautions necessary.

Aromatic and high molecular weight aliphatic acid chlorides have been reacted with alkali cellulose to produce partial esterification. Under these conditions it is necessary to employ excessive amounts of reagent, and the process is, in general, inferior to the pyridine reaction.

Various types of cellulose have been employed as starting materials for cellulose ester preparation, the most commonly used being bleached and purified cotton linters and purified wood cellulose. As a by-product of the cotton industry, linters have been available at reasonable prices and of quality satisfactory for chemical use. The viscosity of solutions of native cotton linters is higher than necessary for esterification and may be adjusted during purification to a suitable value, which may vary according to the esterification process to be used. Wood cellulose for esterification processes must be properly treated to yield a quality approaching that of cotton linters, at the same time preserving uniform chemical reactivity and sufficient viscosity so that esterification conditions will not reduce the viscosity to too low a figure.

Analytical characteristics typical of cotton linters and wood pulp suitable for acetylation are as follows:

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[9] J. F. Haskins and F. Schulze (to Du Pont Rayon Co.), U. S. Patent 1,967,405 (July 24, 1934); *Chem. Abstracts*, **28**, 5982 (1934).

	Cotton linters	Wood pulp
Alpha-cellulose	99%	96%
Solubility in 7.14% NaOH	1.8%	6%
Pentosans	0.8%	1.5%
Ash	0.08%	0.08%
Viscosity in 2.5% cuprammonium hydroxide	5000 cps.	2000 cps.

For preparation of special cellulose esters and, to a considerable extent in experimental investigations, chemically modified celluloses have been used as starting materials because of their increased chemical activity as compared with native celluloses.

Cellulose regenerated from cuprammonium or viscose solutions provides a useful source of raw material lower in viscosity than the native celluloses, and useful for mild reaction conditions. Another form of cellulose very useful for experimental study is that regenerated from cellulose acetate by suspension of the material in aqueous ammonia (15%) for two or three days at room temperature to bring about complete deacetylation. This cellulose has the advantage that it has the chain length of a typical cellulose ester, and can be esterified under mild experimental conditions to produce soluble derivatives.

1. Aliphatic Fatty Acid Esters

(a) CELLULOSE FORMATE

Cellulose formates have been of little interest, either for theoretical study or for commercial use, because of their instability. They are hydrolyzed readily by hot water, and they show a strong tendency toward development of acidity at room temperature in the presence of moisture. Furthermore, the formyl groups are removed completely by dry heating at elevated temperatures, and cellulose is regenerated on such a treatment.[10] Complete esterification with formic acid is very difficult to attain, although it is claimed that, with zinc chloride as a catalyst, the triformate can be made.[11] The usual reaction products contain 20–30% formyl, corresponding to approximately a diformate.[12-14] To obtain these products, the use of swelling agents, such as $ZnCl_2$ or $CaBr_2$, and of catalysts, such as HCl gas, H_2SO_4, and P_2O_5, are recommended; also metal perchlorates, especially magnesium perchlorate, are said to have catalytic activity.[15] The temperature used varies with the catalysts employed, but to prevent degradation of the cellulose, Elöd[13] and Jurling[16] recommended temperatures of 5°C. and below. The physical properties of films and filaments made from these formates have been investigated by Ueda.[17] Mixed acetate formates[18] have been made by reaction of cellulose in the presence of sulfuric acid with the mixed anhydride of acetic and formic acids.

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[10] G. Tocco, *Giorn. chim. ind. applicata,* **13,** 325, 414 (1931).

[11] I. G. Farbenindustrie Akt.-Ges., German Patent 636,307 (Dec. 18, 1936); *Chem. Abstracts,* **31,** 858 (1937).

The formation of cellulose formate containing low percentages of formyl groups is said to be useful as a means of activating cellulose for further esterification with other acids.[19] These formates contain 6–10% formyl and are easily made by soaking the cellulose at room temperature in formic acid of at least 85% strength. Formic acid has been recommended in pretreatment of cellulose prior to acetylation.[20]

(b) CELLULOSE ACETATE

Cellulose acetate is the most widely known organic acid ester of cellulose. It is made at the present time in large commercial quantities for a variety

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[12] Y. Ueda, S. Nakamura, and T. Simada, *Cellulose Ind.* (Tokyo), **15**, 212 (1939); references to earlier papers are included.

[13] E. Elöd, U. S. Patent 1,900,599 (Mar. 7, 1933); *Chem. Abstracts*, **27**, 3073 (1933); Brit. Patent 275,641 (Aug. 9, 1926); *Chem. Abstracts*, **22**, 2273 (1928); French Patent 638,431 (Aug. 29, 1927); *Chem. Abstracts*, **23**, 278 (1929); German Patent 528,148 (June 25, 1931); *Chem. Abstracts*, **25**, 4706 (1931).

[14] W. König (to R. Koepp & Co. Chemische Fabrik Akt.-Ges.), German Patent 657,874 (Mar. 16, 1938); *Chem. Abstracts*, **32**, 6057 (1938).

[15] A. Dobry, French Patent 780,775 (May 3, 1935); *Chem. Abstracts*, **29**, 6056 (1935).

[16] J. G. Jurling, U. S. Patent 1,656,119 (Jan. 10, 1928); *Chem. Abstracts*, **22**, 1040 (1928).

[17] Y. Ueda and T. Simada, *Cellulose Ind.* (Tokyo), **15**, 426 (1939); references to earlier papers are included.

[18] G. W. Seymour and B. B. White (to Celanese Corp. of America), U. S. Patent 2,363,091 (Nov. 21, 1944); *Chem. Abstracts*, **39**, 3158 (1945).

[19] P. A. Chevalet, Brit. Patent 264,181 (Jan. 11, 1926); H. Dreyfus, French Patent 642,329 (Sept. 16, 1927); *Chem. Abstracts*, **23**, 1504 (1929); H. Dreyfus and C. I. Haney, Brit. Patent 288,657 (Apr. 10, 1928); *Chem. Abstracts*, **23**, 703 (1929); I. G. Farbenindustrie Akt.-Ges., Brit. Patent 305,601 (Feb. 5, 1929); *Chem. Abstracts*, **23**, 4819 (1929); R. O. Herzog and G. Frank, French Patent 700,165 (Aug. 7, 1930); *Chem. Abstracts*, **25**, 3481 (1931).

[20] C. I. Haney and M. E. Martin (to Celanese Corp. of America), U. S. Patent 2,391,569 (Dec. 25, 1945); *Chem. Abstracts*, **40**, 2983 (1946).

of uses including the manufacture of cellulose acetate yarn, photographic films, transparent and pigmented sheeting, and plastic compositions such as those used for compression, extrusion, and injection molding, and, to a more limited extent, surface coatings. Annual production of cellulose acetate in the United States has increased rapidly since 1920, as shown in the curve of Figure 13, plotted from estimated data. The product most used is acetone-soluble acetate made by partial hydrolysis of the triester, as first described by Miles in 1905.[21] It is common practice today to refer to the substantially fully esterified ester as the triacetate or primary acetate and to the hydrolyzed product as acetone-soluble acetate or secondary acetate.

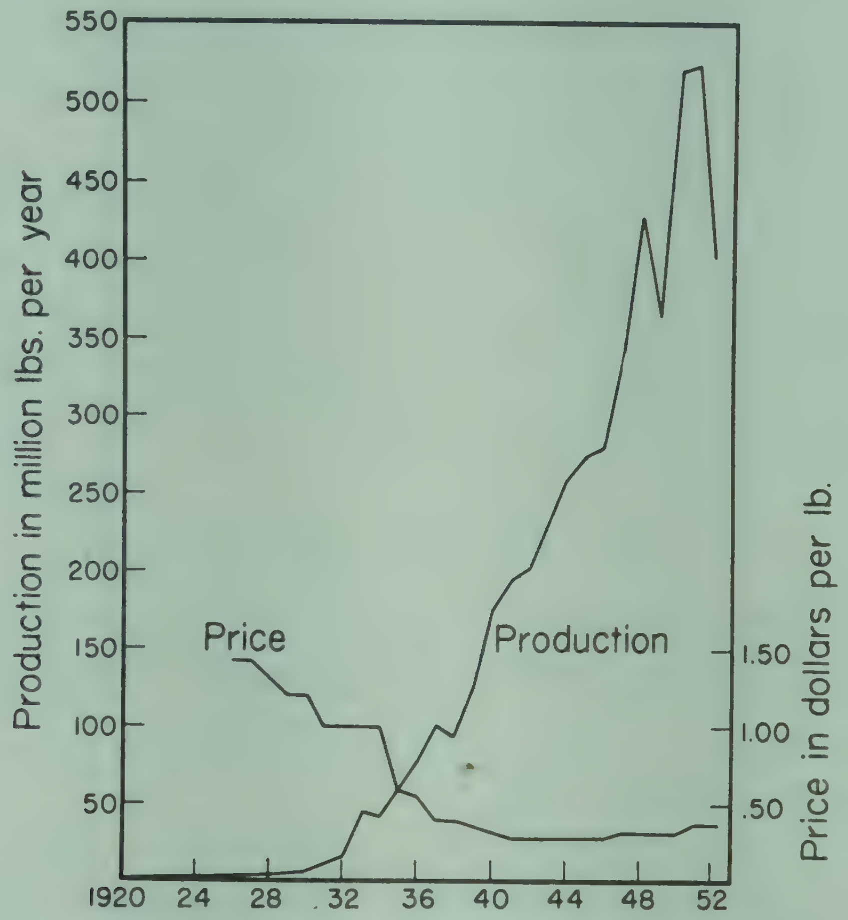

Fig. 13. Production and price of cellulose acetate in the United States since 1920.

The most outstanding technical developments within recent decades have been in the direction of greatly reduced cost of manufacture (Fig. 13), of improved control of processing conditions resulting in better clarity and uniformity of product, and of development of mild conditions of acetylation to prevent excessive degradation of the cellulose, retaining the high molecular structure of the cellulose molecule which contributes to the strength and durability of the product.

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[21] G. Miles, French Patent 358,079 (Dec. 5, 1905).

A continual trend toward milder esterification conditions has been noticeable throughout the history of cellulose acetate. The first reported acetylation of cellulose was accomplished by Schützenberger in 1865[22] by the action of acetic anhydride in a sealed tube at 180°C. The amorphous powder which resulted was soluble in alcohol. Franchimont in 1879[23] used various catalysts to improve the esterification reaction and obtained two types of products distinguished by their solubility in hot or cold alcohol. Later investigations, including those of Cross and Bevan and Miles during the period of 1900–1905, still employed comparatively high acetylation temperatures, although under somewhat more mild conditions than those of Franchimont. The products obtained under these conditions were insoluble in alcohol but soluble in chloroform. Miles distinguished between fully esterified acetate and his new partially hydrolyzed product as, respectively, chloroform-soluble and acetone-soluble derivatives. Later, lower temperatures of esterification were employed, such as those described by Dreyfus,[24] in which the initial esterification mixture is cooled to below 0°C. and during reaction is allowed to increase in temperature to a maximum of 20–30°C., giving a cellulose triacetate insoluble either in chloroform or chloroform–alcohol mixtures. Tetrachloroethane and mixtures of methylene chloride with alcohol are among the few good solvents for this product. Most commercial processes today use esterification temperatures not exceeding 50–60°C.

Numerous catalysts have been recommended for cellulose acetate manufacture, but none has offered outstanding advantages over sulfuric acid. This acid was employed by Franchimont[23] in his early work on cellulose acetylation and has since become the most standard agent for commercial use. A great many patents have been issued describing its use in acetylation procedures. The quantity of catalyst used varies widely, depending upon the temperature of esterification and reactivity of the cellulose employed. Ost[25] compared sulfuric acid and zinc chloride as acetylation catalysts. Quantities of 50–100% of the weight of the cellulose and comparatively high reaction temperatures were required with zinc chloride, whereas sulfuric acid gave good results under mild temperature conditions with 5–10% of the weight of the cellulose. Patents covering the use of these catalysts for cellulose acetate manufacture agree in general with these data.

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[22] P. Schützenberger, *Compt. rend.*, **61**, 485 (1865).

[23] A. Franchimont, *Compt. rend.*, **89**, 711 (1879).

[24] H. Dreyfus, U. S. Patent 1,280,975 (Oct. 8, 1918).

[25] H. Ost, *Z. angew. Chem.*, **32**, 66 (1919).

Perchloric acid is an exceptionally strong esterification catalyst and has been patented for use in acetylation of cellulose.[26] Commercial use of this catalyst, however, has thus far been restricted to the manufacture of fibrous cellulose triacetate. The acid has a purely catalytic action, and does not combine with the cellulose. The fully esterified cellulose acetate is, therefore, of good stability. In solution processes there are no indications of perchloric acid replacing sulfuric acid in commercial use. It is highly corrosive to the metal equipment now used for the preparation of cellulose esters.

Methanesulfonic acid in quantities of at least 50% of the weight of the cellulose[27] is reported to be an effective catalyst for esterification with anhydrides of acids as high as eight carbon atoms. Aromatic sulfonic acids have also been used as esterification catalysts[28] but are not as effective as sulfuric acid.

The effective acidity of a catalyst is the predominant factor in its activity. Since the acetylation reaction is carried out in an anhydrous medium, evaluation of catalysts must be considered from the point of view of nonaqueous systems. The work of Brønsted[29] has shown that ionization must be regarded as related to the solvent system employed. Conant and Hall[30] found that in acetic acid solution a number of amides and other materials, which in aqueous media do not form salts with acids, exhibit salt-forming behavior; these present a system of acid–base equilibria which can be titrated. Measurements of acidities of several mineral acids in glacial acetic acid agree remarkably with their behavior as acetylation catalysts. Sulfuric and perchloric acids in acetic acid solution were termed superacid solutions because of their exceptional strength as compared with other acids. Hydrochloric, phosphoric, and nitric acids in glacial acetic are comparatively weak, as are the organic sulfonic acids.

Sulfuric acid undergoes chemical changes in the presence of acetic anhydride. Franchimont[31] reported that sulfoacetic acid is formed by action of acetic anhydride and assumed that acetylsulfuric acid is an intermediate product. Stillich[32] showed that acetylsulfuric acid is readily formed at low temperatures; at elevated temperatures, in the presence of an excess of acetic anhydride, quantitative conversion to sulfoacetic acid takes place. Van Peski[33] studied the reactions of acetic and sulfuric acids in detail and prepared acetylsulfuric acid.

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[26] C. J. Malm (to Eastman Kodak Co.), U. S. Patent 1,645,915 (Oct. 18, 1927); *Chem. Abstracts*, **22**, 164 (1928); D. Krüger and F. Höhn, German Patent 519,877 (Nov. 5, 1931); *Chem. Abstracts*, **25**, 3481 (1931).

[27] Société des usines chimiques Rhône-Poulenc, French Patent 705,546 (June 9, 1931); *Chem. Abstracts*, **25**, 5287 (1931).

[28] H. S. Mork, A. D. Little, and W. H. Walker, U. S. Patent 709,922 (Sept. 30, 1902); French Patent 324,862 (Dec. 27, 1902).

[29] J. N. Brønsted, *Ber.*, **61B**, 2049 (1928).

[30] J. B. Conant and N. F. Hall, *J. Am. Chem. Soc.*, **49**, 3047 (1927).

[31] A. Franchimont, *Compt. rend.*, **92**, 1054 (1881).

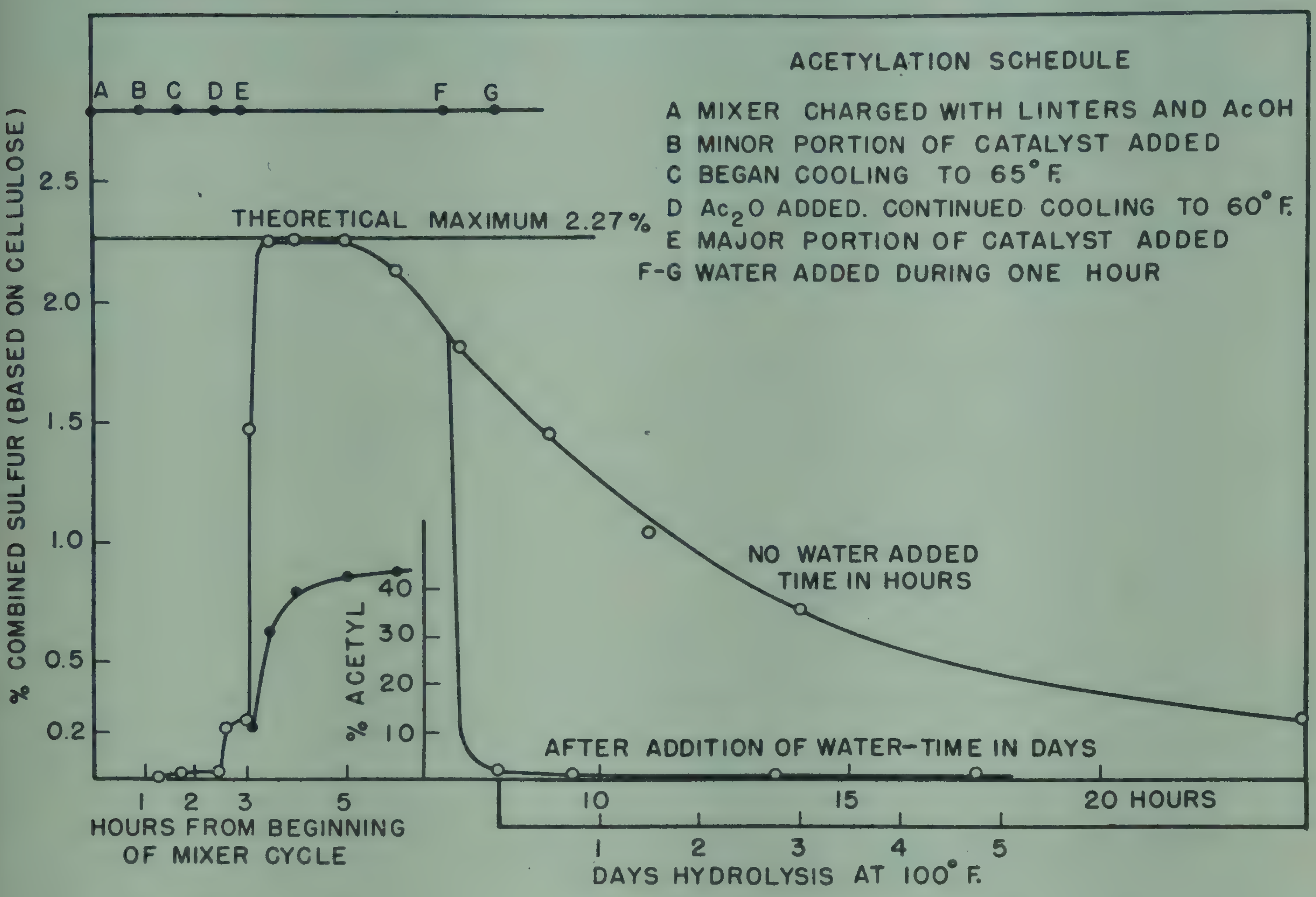

Fig. 14. Combined sulfur during preparation of cellulose acetate (Malm, Tanghe, and Laird[34]).

Under normal acetylation conditions there is practically no conversion of acetylsulfuric acid to sulfoacetic acid. In the first part of the acetylation, when the sulfuric acid and acetic anhydride concentrations are high enough for this reaction, the temperature is low. Also, in a short time the sulfuric acid combines quantitatively with the cellulose, as has been shown by Malm, Tanghe, and Laird.[34] During the acetylation reaction it is replaced by acetic acid through transesterification and reacts with other available hydroxyl groups in the cellulose. After all the hydroxyl groups have been esterified, the transesterification continues and the amount of combined sulfuric acid decreases. This is shown in Figure 14.

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[32] O. Stillich, *Ber.*, **38**, 1241 (1905).

[33] A. J. Van Peski, *Rec. trav. chim.*, **40**, 103 (1921).

[34] C. J. Malm, L. J. Tanghe, and B. C. Laird, *Ind. Eng. Chem.*, **38**, 77 (1946).

The sulfation reaction is preferential to the primary OH groups.[34a] At the end of the esterification most of the bound sulfuric acid is combined with primary OH groups. This is shown[34a] (Fig. 15) by extending an esterification and comparing the combined sulfur of samples with the primary and secondary OH content (determined by tritylation and carbanilation) of samples from which the combined sulfuric acid had been removed by selective hydrolysis.

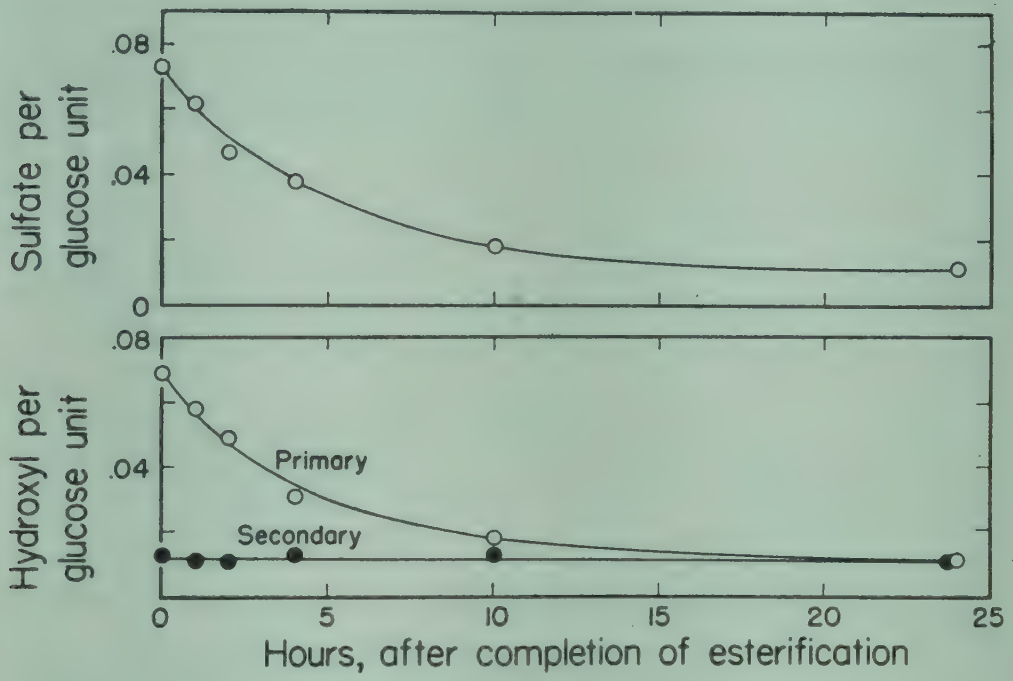

Fig. 15. Preferential combination of sulfuric acid with primary hydroxyl groups in cellulose acetate.

Combined sulfuric acid results in very poor stability of cellulose acetate and must be reduced to an insignificant quantity in the final product. In the manufacture of cellulose acetate the acetylation is interrupted when only a small amount of the combined sulfuric acid has been replaced by acetyl through transesterification. This is done by adding water in the form of aqueous acetic acid of 50–75% strength. Most of the combined sulfuric acid can be removed at this point by adding the water at a high enough temperature and at a slow enough rate. This is shown in Figures 16 and 17.[34]

If the cellulose acetate is to be used as the substantially fully esterified product, this addition of water is very critical and determines the stability of the ultimate product. If, however, the acetate is to be hydrolyzed to an acetone-soluble product, the combined sulfuric acid is also removed during the hydrolysis, and the amount combined in the final product is influenced by the sulfate-ion concentration during the hydrolysis. To keep this concentration low when large quantities of sulfuric acid have been used as catalyst during the acetylation, metal ions such as magnesium can be added with the water. These form insoluble sulfates with part of the sulfuric acid, thereby removing some of the sulfate ions from the solution.[35] If the combined sulfuric acid content still is too high for satisfactory stability at the time of precipitation, several methods can be used for its removal.

[34a] C. J. Malm and L. J. Tanghe, paper presented before the XIIIth International Congress of Pure and Applied Chemistry, Stockholm, Sweden, August, 1953.

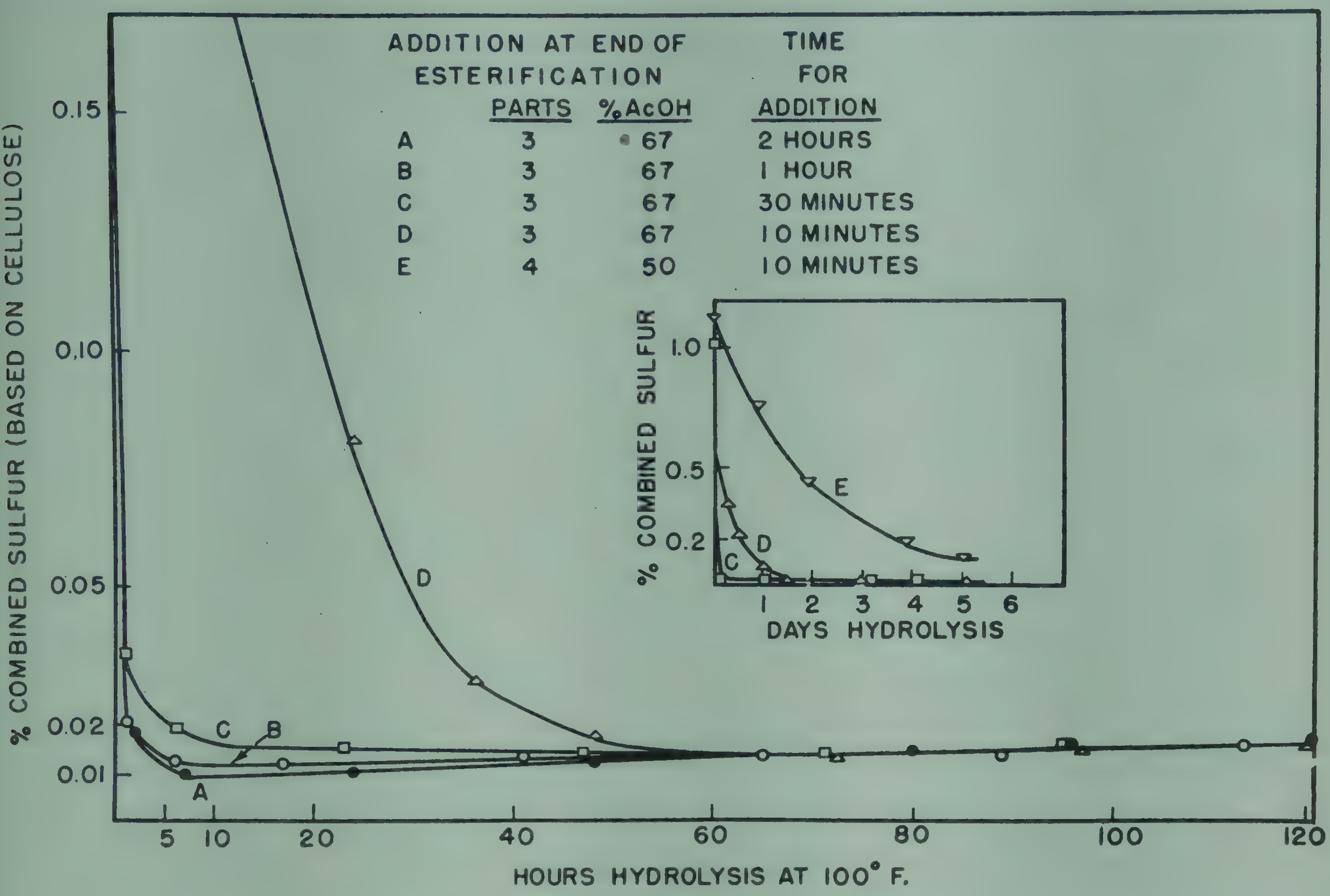

Fig. 16. Sulfur content during hydrolysis of cellulose acetate after addition of water at different rates (Malm, Tanghe, and Laird[34]).

Boiling water has often been recommended as an effective stabilization treatment. Modifications designed to give improved results include use of superheated steam[36] instead of boiling water, or treatment in an autoclave to permit use of higher temperatures.[37] Boiling water acidified with either organic or mineral acids has also been recommended as a stabilization treatment.[38] In all of these treatments, the essential requirement is removal of sulfate without appreciable hydrolysis of acetyl groups. The sulfate groups are quite readily removed by boiling water if the combined

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[35] C. L. Fletcher (to Eastman Kodak Co.), U. S. Patent 2,259,462 (Oct. 21, 1941); *Chem. Abstracts*, **36**, 655 (1942); H. Dreyfus, Brit. Patent 566,863 (Jan. 17, 1945); *Chem. Abstracts*, **41**, 1435 (1947).

[36] C. Dreyfus and H. Martin (to Celanese Corp. of America), U. S. Patent 2,071,333 (Feb. 23, 1937); *Chem. Abstracts*, **31**, 2816 (1937).

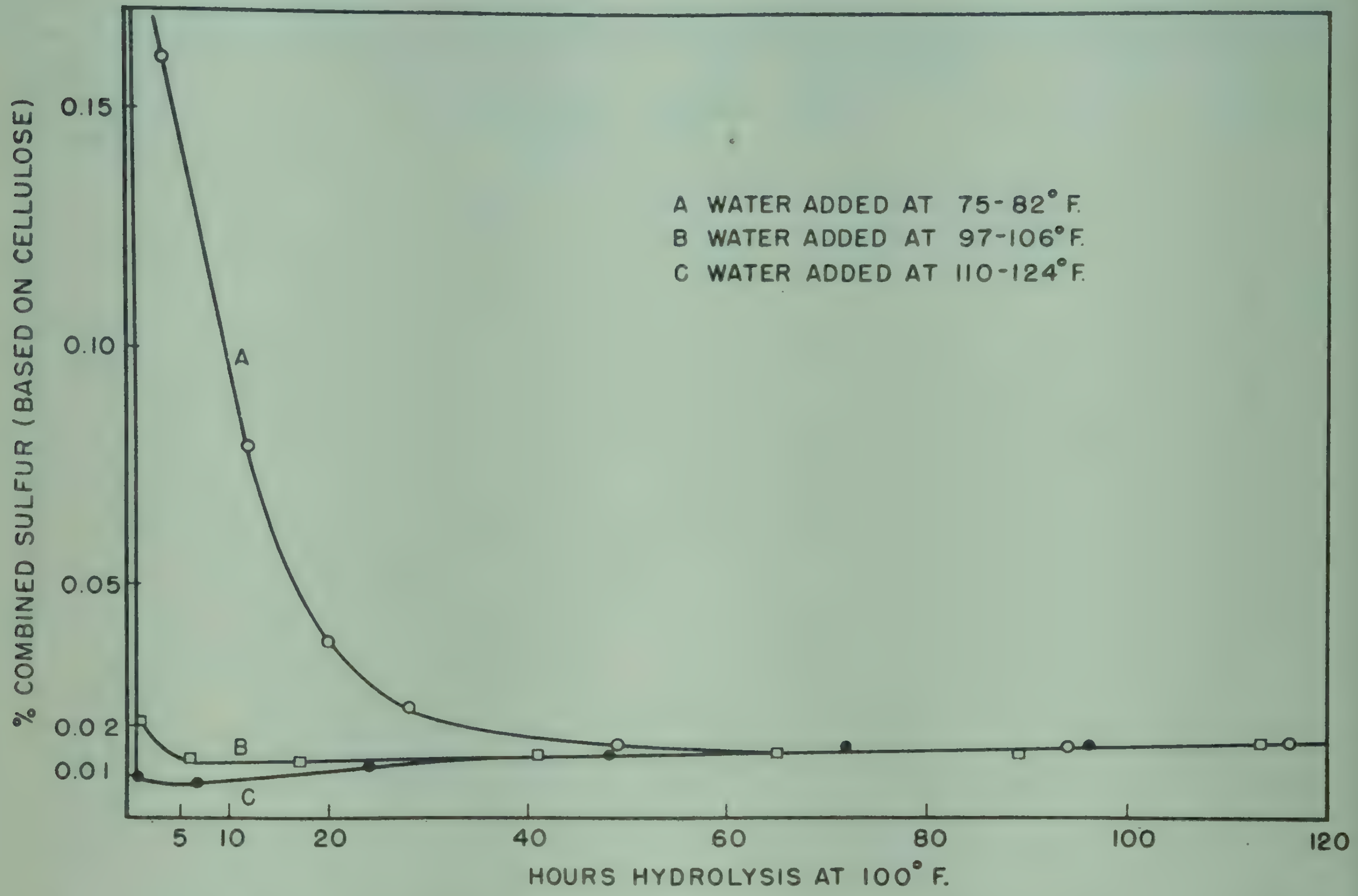

Fig. 17. Sulfur content during hydrolysis of cellulose acetate after addition of water at different temperatures (Malm, Tanghe, and Laird[34]).

sulfuric acid is in the form of an acid rather than a salt. Should the unstable product be given an opportunity to react with sodium or potassium salts before stabilization, the action of boiling water is comparatively ineffective, since alkali metal salts of the cellulose sulfate are very resistant to hydrolysis. If left in the final product the sulfuric acid, even if partially neutralized with alkali metals, leads to instability toward heat.

Salts of alkaline earth or heavier metals may be used to neutralize the acidity of the combined sulfate and give stable products. Magnesium salts have been recommended, as have those of calcium, barium, and aluminum. These may be used in just sufficient quantity to neutralize the sulfate, or may be added in excess and allowed to remain on the product. Such treatments result in increased ash content of the product and in some cases affect the clarity of its solution. They also have a distinct effect on the viscosity of the acetate in nonpolar solvents.[39]

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[37] A. Aktien and H. Schulz (to Wolff and Co.), German Patents 440,844 (Feb. 12, 1927); 511,020 (July 10, 1930); *Chem. Abstracts*, **25**, 1379 (1931).

[38] I. G. Farbenindustrie Akt.-Ges., Brit. Patent 299,326 (Mar. 24, 1930); *Chem. Abstracts*, **23**, 3343 (1929).

(*1*) *Solution Process*

Except for a small amount of cellulose triacetate which is made by the fibrous process, all cellulose acetate is manufactured by the solution process. Sulfuric acid is the most commonly used catalyst and the discussion below will be confined to the use of this catalyst.

Acetylation of cellulose is a heterogenous reaction, the cellulose being suspended in the reaction medium and passing gradually into solution after esterification has taken place. The course of the reaction has been found by Sakurada[40] to be largely controlled by rates of diffusion of reactant and catalyst into the cellulose fiber. Hess and Trogus[41] have observed changes in x-ray diagrams from that of cellulose to that of the reaction product. After the initial surface esterification, the reaction depends upon diffusion of reactant and catalyst into the inner part of the fiber. The physical condition of the cellulosic material is thus of primary importance to the quality of the product. Only under conditions of uniform reaction can products free from insoluble particles, unesterified fiber, and hazy appearance in solution be obtained. Ideal esterification conditions are obtained if the cellulose is not dried but the water is removed with acetic acid. This might, however, not be economically practical. If the cellulose is dried prior to acetylation, the drying should be carried out to avoid high temperatures and local over-drying. Removal of the last few per cent of moisture increases greatly the resistance of the fibers to acetylation.

(*a*) *Pretreatment.* The cellulose is usually given an activation treatment before the acetylation. Of the many modifications which have been recommended, the most common is treatment with acetic acid either alone or in the presence of part or all of the esterification catalyst. In an early patent, Wohl[42] described steeping cellulose in acetic acid and then pressing out the excess liquid before acetylation. Hot acetic acid[43] and its vapors[44] have also been patented as pretreatment agents. Use of catalysts in the pretreatment step is included in many process modifications. Aqueous acetic acid is more effective than glacial in producing a reactive cellulose,[45] but, inasmuch as any water remaining from pretreatment must later be destroyed by additional anhydride, glacial acid is usually used. The quantity of pretreatment acid may vary widely, according to the convenience of the process employed.

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[39] C. J. Malm, L. J. Tanghe, and G. D. Smith, *Ind. Eng. Chem.*, **42**, 730 (1950).

[40] I. Sakurada, *J. Soc. Chem. Ind., Japan*, **35**, Suppl. binding 3, 283 (1932).

[41] K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1931).

[42] A. Wohl, Brit. Patent 20,527 (July 17, 1913); French Patent 448,072 (Jan. 22, 1913).

Although the temperature of pretreatment may range from 20°C. to the boiling point of acetic acid (118°C.) or above, it is usually maintained below 50°C. to avoid losses through evaporation. In the absence of catalyst, this treatment causes only slight reduction of viscosity of the cellulose. In the presence of catalyst, the cellulose viscosity drops rapidly. Cellulose employed for acetylation has usually many times the viscosity it is to possess after acetylation, and at some step in the process the viscosity will be greatly reduced. Werner[46] has studied the reduction of viscosity during esterification. This action is brought about by the catalyst; it will occur mainly in the pretreatment step if catalyst is present, and will also take place simultaneously with acetylation.

The amount of activation which is necessary depends upon the previous history of the cellulose and the amount of catalyst used in the acetylation. Increases in temperature and time during the activation with acetic acid increase the efficiency of the activation. Decrease in ratio of acetic acid to cellulose will also increase the efficiency. This is due to the greater effect of the moisture in the cellulose on the concentration of the acetic acid.

(*b*) *Acetylation.* High reactivity of cellulose toward acetylation is obtained when there is rapid and uniform sorption of sulfuric acid. The amount of sorbed catalyst is not as important as the uniformity of its distribution in the cellulose.[46a] The acetylation takes place much slower than the sulfation. Here again it is found that the primary hydroxyl groups react more readily than the secondary.[46b] The acetylation of cellulose should be allowed to proceed sufficiently slowly so that the reaction temperature can be controlled, and, since the reaction is accompanied by evolution of a considerable quantity of heat, the esterifying anhydride must be added at a comparatively low temperature. This will vary in different processes, the degree of cooling required being in general dependent upon the amount of catalyst used and the desired viscosity of the final product.

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[43] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patents 1,668,944–5 (May 9, 1928); *Chem. Abstracts*, **22**, 2272 (1928).

[44] H. Dreyfus, Brit. Patent 263,939 (Jan. 6, 1927); *Chem. Abstracts*, **22**, 164 (1928).

[45] H. Dreyfus, Brit. Patent 343,986 (Feb. 16, 1931); *Chem. Abstracts*, **26**, 303 (1932).

[46] K. Werner, *Cellulosechemie*, **12**, 320 (1931).

[46a] C. J. Malm, K. T. Barkey, D. C. May, and E. B. Lefferts, *Ind. Eng. Chem.*, **44**, 2904 (1952).

[46b] C. J. Malm, L. J. Tanghe, B. C. Laird, and G. D. Smith, *J. Am. Chem. Soc.*, **75**, 80 (1953).

An amount of acetic anhydride, somewhat in excess of that necessary to esterify the cellulose and to take care of any moisture present at the end of the pretreatment, is added after the cooling operation has brought the temperature to the proper point, and, if the catalyst has not been previously added to aid in pretreatment, it must also be introduced at this time.

During the early stages of acetylation, the reaction should be well controlled by external cooling to prevent too rapid a temperature rise. As the reaction proceeds, it may be allowed to increase gradually in temperature to a maximum, which should be well controlled to insure proper viscosity of product. Proper correlation of the initial speed of reaction, maximum temperature, and total time of esterification is important in production control and must be maintained in balance.

Complete solution of the cellulose indicates the end of the esterification reaction, and the temperature is then held constant until the solution viscosity, which drops slowly under these conditions, is found by control test to be at the proper point. Care must be taken not to allow the reaction to continue for too long a time after acetylation is completed if small catalyst concentrations are employed, since gelling will take place.

This gelling is caused by the insolubility in acetic acid or acetic acid–acetic anhydride of a triacetate of high molecular weight cellulose. It can be avoided by uniformly breaking down the cellulose before the acetylation or by using large enough quantities of sulfuric acid as catalyst. A fully esterified cellulose acetate sulfate of high combined sulfuric acid content is soluble in the acetylation mixture. However, as the combined sulfuric acid is being replaced by acetyl through transesterification at the end of the esterification, the solubility decreases and ultimately gelling occurs.

(*c*) *Hydrolysis.* The acetylation reaction is stopped by the addition of sufficient water to destroy any acetic anhydride remaining in the reaction mixture and to bring the water content of the solution usually to 5–30%. The water is best added in the form of aqueous acetic acid to prevent precipitation of the cellulose acetate. During the addition of this solution, there is considerable removal of combined sulfate. This is especially effective if the temperature is above 40°C. and the addition is slow. (See Figs. 16 and 17.) There is a critical water concentration at which the combined sulfate is removed most efficiently.[46c] The exact optimum concentration depends upon the amount of free sulfuric acid present and changes as the sulfuric acid is split off.[34a]

Further quantities of sulfuric acid may be added with the aqueous acetic solution, if this is desirable to speed up the hydrolysis step which is to follow. Neutralizing agents may be added if large amounts of sulfuric acid were employed in the esterification.

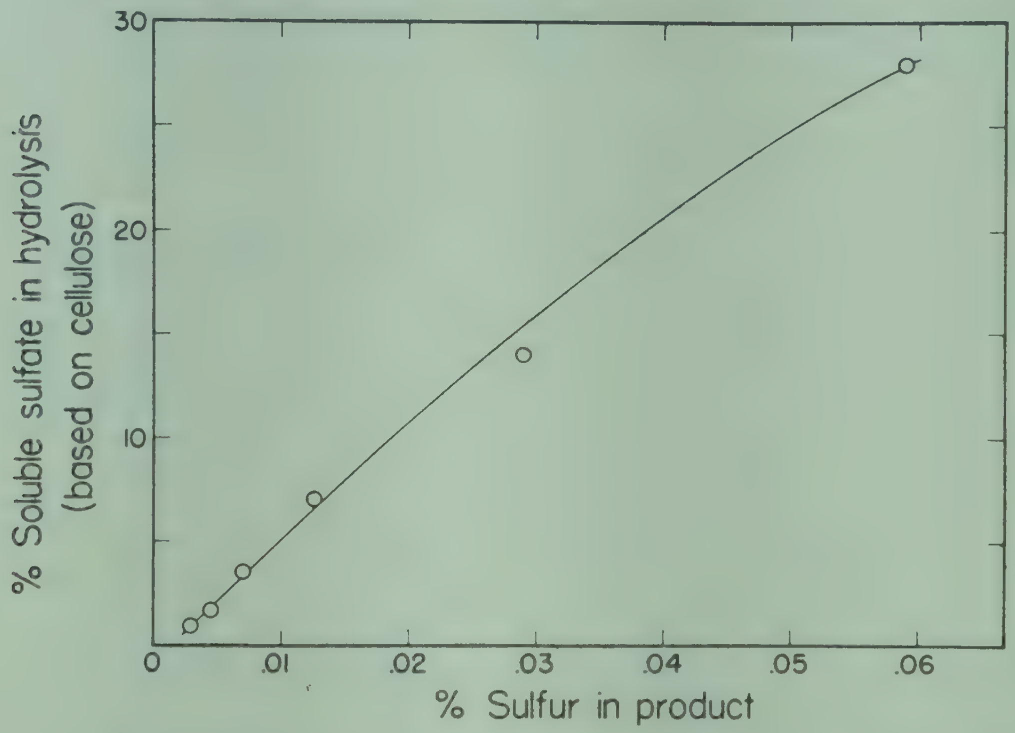

Fig. 18. Relation between soluble sulfate and combined sulfur in cellulose acetate.

The amount of combined sulfur in the product depends upon the concentration of soluble sulfate in the hydrolysis mixture[34a] (Fig. 18) and the degree of hydrolysis (Fig. 16). The combined sulfur content passes through a minimum during the hydrolysis and increases then slowly due to the increase in the concentration of cellulose hydroxyl groups in the hydrolysis mixture.[34a]

The reaction solution, as obtained after addition of the aqueous acetic acid, undergoes an acid hydrolysis to remove some of the acetyl groups. In order that this be a uniform reaction, it is necessary to maintain uniform temperature until the desired degree of hydrolysis has been obtained. This temperature may be chosen to suit the equipment and convenience of the process, the rate of reaction for a given concentration of catalyst being faster, the higher the temperature is.

The higher the percentage of water in the hydrolysis solution, the less will be the degradation at a given temperature. The susceptibility of the acetate to degradation increases with decrease in acetyl content; therefore if a rapid hydrolysis with large quantities of sulfuric acid or at high temperatures is desired, water should be added during the process.[47] Hydrolysis under ordinary conditions may be carried to as low as 30% acetyl. At about this point the usual reaction solutions containing approximately 10% water become poor solvents for the acetate, and gelatinous precipitation begins to take place. By addition of larger quantities of water to reduce the acetic acid strength to 60 or 70%, the hydrolysis may be continued to acetyl values below 20%, at which point the product becomes completely water-soluble (see Fig. 25) and must be isolated by precipitation into organic solvents such as acetone or alcohol.[48] Continued hydrolysis below about 13% acetyl results in regeneration of essentially deacetylated cellulose, which is insoluble in water and organic solvents.

[46c] T. Araki, *Textile Research J.*, 20, 631 (1952).

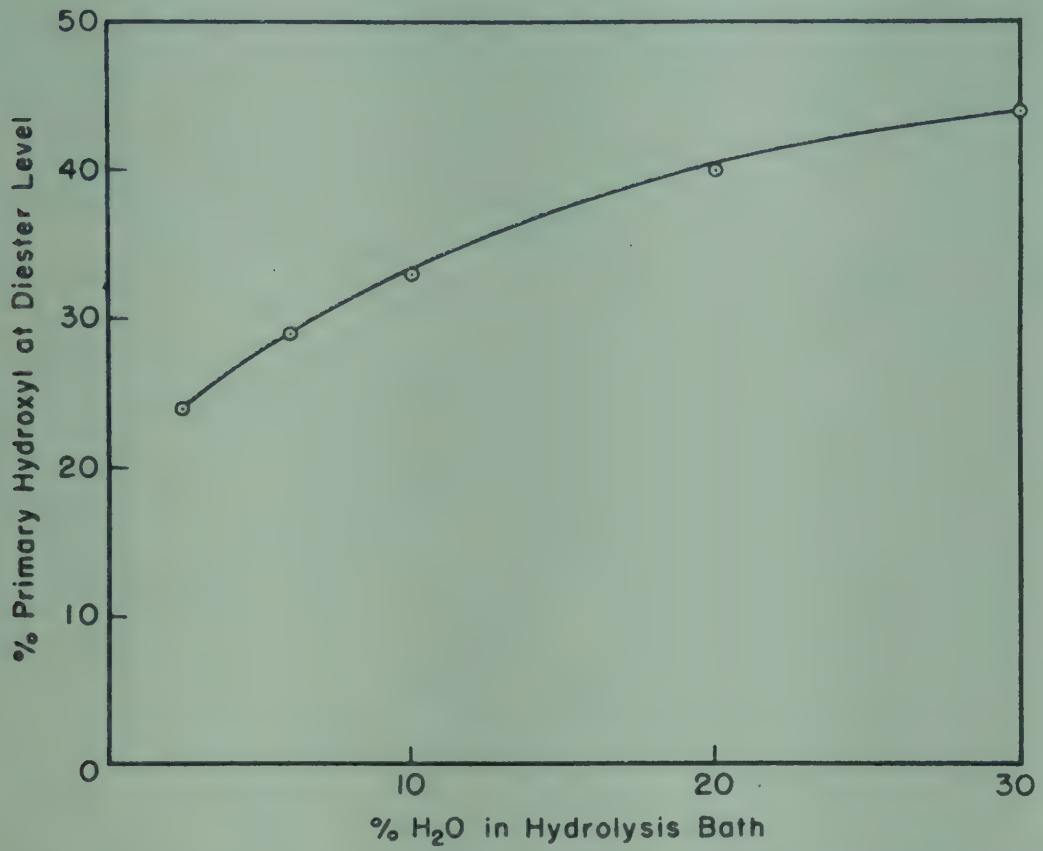

Fig. 19. Effect of water content on per cent primary hydroxyl (Malm, Tanghe, and Laird[49]).

The percentage of water in the hydrolysis bath influences the ratio of primary to secondary hydroxyl groups in the acetate.[49] (See Fig. 19.)

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[47] C. J. Malm and C. L. Fletcher (to Eastman Kodak Co.), U. S. Patent 2,013,830 (Sept. 10, 1935); *Chem. Abstracts,* **29,** 7074 (1935).

[48] C. R. Fordyce (to Eastman Kodak Co.), U. S. Patent 2,129,052 (Sept. 6, 1938); *Chem. Abstracts,* **32,** 8777 (1938).

[49] C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Am. Chem. Soc.,* **72,** 2674 (1950).

This is due to partial preferential re-esterification of primary hydroxyl groups during the hydrolysis. An increase in the acetic acid concentration promotes the re-esterification and results in a product of lower primary hydroxyl content.[49a,49b]

During the course of the hydrolysis, test samples may be taken, by which the time of hydrolysis to give any desired acetyl value may be determined.

If an ester of high purity and clarity is desired, the solution can be filtered before precipitation. This can be done by neutralizing the sulfuric acid with magnesium acetate under conditions which form the right-size magnesium sulfate crystals and using these as a filter aid.[50]

(*d*) *Purification.* At the time when control tests have indicated that the proper degree of hydrolysis has been reached, the cellulose acetate is precipitated from solution.

The most important objects in this operation are to produce a precipitated material which is readily penetrated by water so that it may be easily washed to remove all uncombined acids, and to obtain, for recovery, acetic acid of as high concentration as possible. A stream of viscous solution poured into water will usually result in formation of "skins" of precipitated material containing entrapped solution into which it is difficult for water to penetrate. For this reason, if solutions are precipitated directly into water, they must first be diluted to a low viscosity. A more practical procedure for commercial use is to precipitate the solution into dilute acetic acid, keeping the concentration of the precipitation acid within a range of 25 to 35% acetic acid by simultaneous addition of reaction solution and dilute acid.[51]

If the ester is desired in a powder form, the precipitation can be carried out by diluting the solution with an acetic acid–water mixture and finally adding an acid–water mixture of sufficient water concentration to cause precipitation. The amount of dilution, strength of acid, and temperature

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[49a] C. J. Malm, L. J. Tanghe, B. C. Laird, and G. D. Smith, *J. Am. Chem. Soc.*, **74,** 4105 (1952).

[49b] L. A. Hiller, Jr., *J. Polymer Sci.*, **10,** 385 (1953).

[50] H. G. Reed and J. K. Beasley (to Eastman Kodak Co.), U. S. Patent 2,494,143 (Jan. 10, 1950); *Chem. Abstracts*, **44,** 2806 (1950); M. E. Martin and T. M. Andrews (to Celanese Corp. of America), U. S. Patent 2,522,580 (Sept. 19, 1950); *Chem. Abstracts*, **45,** 1343 (1951).

[51] H. T. Clarke (to Eastman Kodak Co.), U. S. Patent 1,823,348 (Sept. 15, 1931); *Chem. Abstracts*, **26,** 304 (1932); French Patent 693,133 (Nov. 17, 1930); *Chem. Abstracts*, **25,** 1671 (1931); Brit. Patent 342,596 (Feb. 5, 1931); *Chem. Abstracts*, **25,** 4401 (1931).

of precipitation have to be varied, depending upon the viscosity of the ester and its acetyl content, to obtain optimum results.[52]

The process of washing must be given careful consideration in commercial operation because it is necessary to recover the acetic acid. The cost of recovery increases rapidly with increased dilution. The original precipitation liquor is first drained off, and means are then employed to remove as much as possible of the acid held by the cellulose acetate with as little further dilution of the acid as possible. After this has been accomplished, the product is thoroughly washed with water to remove the last traces of acetic acid and catalyst.

The quality of water employed for washing is important to the quality of the product. Good clarity and freedom from color can be obtained only by use of clear water free from iron and other color-causing substances.

The final operation in cellulose acetate manufacture is drying. The last wash water is removed by a centrifuge, press, or similar equipment, and the product is dried.

The recovery of used acetic acid, mentioned above as an essential step in cellulose acetate manufacture from an economic point of view, is rendered difficult by the fact that vapor pressure relationships prevent easy separation of water and acid by fractional distillation. Early recovery methods involved evaporation to obtain sodium acetate. Present processes, however, use extraction or azeotropic distillation.

The following procedure[34] will serve as an example of the solution process:

One part of cellulose, moisture content about 5%, is added to 2.4 parts of acetic acid in a Werner and Pfleiderer type stainless steel mixer and the mixer is run for one hour at 37.8°C. (100°F.). Four parts of acetic acid and 0.88% H_2SO_4, based on the weight of the cellulose, are added, and the mixing is continued at the same temperature for 45 minutes before cooling to 18.3°C. (65°F.). Next, 2.7 parts of 98% acetic anhydride are added, and the cooling is continued to 15.6°C. (60°F.). Then 6.12% H_2SO_4, based on the weight of the cellulose, diluted with an equal weight of acetic acid is added. The temperature is permitted to rise gradually to 32–35°C. (90–95°F.). during an interval of 1.5 to 2 hrs. At this stage the reaction mixture is very viscous and free from fibers. A mixture of one part of water and two parts of acetic acid is then added during an interval of 1 hr. The reaction of the excess anhydride with the water gives a sharp temperature rise of about 5°C. (10°F.). After the solution has been thoroughly mixed and the temperature adjusted to 37.8°C. (100°F.), the solution is transferred to a hydrolysis vessel and held at 37.8°C. (100°F.) until an ester of the desired acetyl content is obtained.

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[52] C. J. Malm and C. L. Crane (to Eastman Kodak Co.), U. S. Patent 2,469,395 (May 10, 1949); *Chem. Abstracts*, **43**, 5592 (1949).

(2) *Modified Solution Processes*

Numerous variations of procedure for the manufacture of cellulose acetate have appeared in the patent literature. A great many of these are concerned with details of processes essentially as described above. A few involve major changes and are worthy of note.

Zinc chloride as catalyst has been employed on a production scale. Its advantages lie in better solubility of the triacetate in an acetic acid–zinc chloride mixture, which prevents gelling, and in good stability of the resulting product. The presence of zinc chloride in the precipitation liquor, however, complicates the recovery of acetic acid.

Several solvents other than acetic acid have been recommended for acetylation media, but of these only the chlorinated hydrocarbons[53] and sulfur dioxide are of commercial interest. Of the chlorinated solvents, methylene chloride is being used on production scale. Its excellent solvent power for cellulose triacetate makes it possible to obtain products of very high viscosity with low catalyst concentration, which in an acetic acid reaction solution would result in gelling. The small amount of catalyst is advantageous in giving only minor quantities of combined sulfate in the product. Methylene chloride, because of its low boiling point, can be used to control the acetylation reaction temperature by evaporation.[54] This makes it possible to use much larger batch sizes than are possible when the reaction temperature is controlled by cooling of the mixer jacket only.

The following procedure[55] will serve as an example of the process which uses methylene chloride as a solvent:

> The acetylation is carried out in a horizontal cylindrical vessel provided with stirring blades on a horizontal shaft. This acetylator is fully charged with cellulose; then the reaction mixture, previously cooled to 15–20°C., is added in two or more portions. The reaction mixture consists of 1 part H_2SO_4, 400 parts of methylene chloride, and 300 parts of acetic anhydride (95% or over) per 100 parts of cellulose. The temperature is not allowed to exceed 50°C. Under these conditions esterification to triacetate is completed in a reaction time of 5 to 6 hrs.

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[53] R. Hofmann (to Hercules Powder Co.), U. S. Patent 2,126,190 (Aug. 9, 1938), *Chem. Abstracts*, **32**, 7723 (1938); Brit. Patent 337,366 (Oct. 27, 1930); *Chem. Abstracts*; **25**, 2288 (1931); French Patent 697,156 (Jan. 13, 1931); *Chem. Abstracts*, **25**, 2848 (1931); German Patent 526,479 (June 6, 1931); *Chem. Abstracts*, **25**, 4401 (1931); H. LeB. Gray (to Eastman Kodak Co.), U. S. Patent 1,823,359 (Sept. 15, 1931); *Chem. Abstracts*, **26**, 304 (1932).

[54] L. E. Clement (to Eastman Kodak Co.), U. S. Patent 2,104,023 (Jan. 4, 1938); *Chem. Abstracts*, **32**, 1931 (1938).

[55] Office of the Publication Board, PB Report 377, Continuous and Staple Fiber Plants of Germany, 1945.

The contents of the acetylator are then discharged into the hydrolyzing and precipitating vessel. There is then added 50 parts of water and 6.5 parts of sulfuric acid per 100 parts of the original cellulose and the ester is hydrolyzed to the desired extent at 55° to 60°C. Hydrolysis is stopped by addition of 20 parts of a 30% solution of sodium acetate, whereupon the methylene chloride is removed by distillation and recovered. The temperature is ultimately raised to 80°C. in order to maintain the residue, a 30% solution of cellulose acetate in acetic acid, in a fluid state. At this temperature the acetate is precipitated by adding 800 parts of an acetic acid solution of 5 to 12% concentration, the exact concentration depending upon the type of acetate made. The acetate is then washed and dried in the customary way.

Sulfur dioxide is a good solvent for cellulose acetate and has been employed as a reaction solvent in a process which has been tried on a commercial scale.[56] Into a closed reaction vessel containing the cellulose, a solution of acetic anhydride, liquid sulfur dioxide, and sulfuric acid catalyst is introduced under suitable pressure. The reaction temperature is conveniently controlled by pressure variation to permit necessary evaporation of sulfur dioxide, which is returned to the reaction chamber by reflux condensation. Excessive heat of reaction is readily absorbed by this type of "internal refrigeration." Hydrolysis to acetone solubility[57] may be carried out in the customary way by adding enough water to destroy excess acetic anhydride and to supply 3–10% water to the reaction mixture, and, if desired, by supplying additional sulfuric acid to increase the speed of hydrolysis.

(3) *Fibrous Acetylation Processes*

If a sufficient quantity of a liquid component which is not a solvent for cellulose acetate is included in an acetylation bath, the reaction product may be prevented from dissolving, so that a fibrous esterification results. Such reactions proceed in much the same manner as in the solution methods. Similar temperatures and catalyst concentrations are used, but usually larger proportions of liquid to cellulose are necessary because of the bulk of the fibrous material as compared with equal amounts in viscous solution.

In an early process of this type, Lederer[58] employed carbon tetrachloride as the inert component. Aromatic hydrocarbons are the liquids most commonly recommended for use, although other inert diluents such as ethers and aliphatic hydrocarbons, which do not react with acetic anhydride or interfere with the action of the catalyst, may be employed. The value of a nonsolvent depends largely upon its ability to maintain the cellulose in a swollen and easily penetrable condition throughout the esterification, while at the same time preventing dissolution. Thus, when aliphatic hydrocarbons are used, an auxiliary solvent, such as methylene chloride, ethylene chloride, or sulfur dioxide, improves the speed of the reaction and the uniformity of the resulting product.

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[56] L. M. Burghart (to U. S. Industrial Alcohol Co.), U. S. Patent 1,816,564 (July 28, 1931); *Chem. Abstracts*, **25**, 5557 (1931).

[57] L. M. Burghart (to U. S. Industrial Alcohol Co.), U. S. Patent 1,822,563 (Sept. 8, 1931); *Chem. Abstracts*, **25**, 5990 (1931).

[58] L. Lederer, U. S. Patent 999,236 (Aug. 1, 1911); *Chem. Abstracts*, **5**, 3156 (1911); Brit. Patent 3103 (Feb. 7, 1907); *Chem. Abstracts*, **1**, 2649 (1907).

The fibrous process is of interest only if a fully esterified cellulose acetate is desired. Due to the difficulties of removing combined sulfuric acid from a fully esterified product, perchloric acid is the preferred catalyst in this process.

No method of hydrolysis in suspension has yet proved sufficiently successful to achieve commercial use. Fibrous products which are somewhat less than fully esterified may be prepared by processes of Sindl and Frank[59] in which large quantities of sulfuric acid catalyst are employed under conditions which encourage high cellulose sulfate formation. The product is then treated with esters, such as ethyl acetate, at elevated temperatures to remove the sulfate, leaving unesterified hydroxyl groups.

The following esterification procedure[60] serves as an example of the fibrous acetylation process:

> The esterification is carried out in a perforated stainless steel drum which rotates inside a stainless steel container. Into this drum is fed 313 kg. (dry weight) of cellulose conditioned to a moisture content not greater than 7%. Then 15 times this weight of acetic acid containing 14% acetic anhydride is added. The internal drum is meanwhile rotating at 6 r.p.m. and continues to do so for 2 hrs. The excess liquid is then removed by rotating the drum at 370 r.p.m.; 750 kg. of the pretreatment liquors are left on the cellulose.
>
> The acetylation liquor consists of 65% acetic acid, 18.5% benzene, and 16.5% acetic anhydride.
>
> The catalyst is 70% perchloric acid, and between 1 and 2% (based upon the weight of the cellulose) is used depending upon the quality of the cellulose. Into the drum rotating at 6 r.p.m. is run 3200 liters of the acetylation liquor previously cooled to −18° to −25°C. The temperature is allowed to rise slowly and reaches 27–29°C. in about 1–1.5 hrs. The conditions are adjusted so that the acetylation is complete in about 6 hrs. For low viscosity the maximum temperature is 35°C.; for medium viscosity, 30°C.; and for high viscosity, 26°C. Throughout the whole acetylation the acetylating liquors are kept circulating.
>
> As soon as a sample just dissolves in a mixture of methylene chloride–methanol (9:1 by volume), 600 liters of benzene containing 3% acetic acid is run in. This addition is made

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[59] O. Sindl and G. Frank, U. S. Patent 2,134,332 (Jan. 10, 1939).

[60] British Intelligence Objectives Subcommittee, London, B.I.O.S. Final Report 1859, Item 21, *Manufacture of Cellulose Triacetate, Yarn and Films* (Feb. and March, 1948).

about 1 hr. after the commencement of the acetylation and prevents the acetylated product from swelling and partially dissolving during the later stages.

After the reaction is completed, another 1200 liters of benzene is added and the catalyst is "killed" by the addition of 3 kg. of potassium carbonate in 30 kg. of acetic acid. The circulation is continued about 0.5 hr. until the specific gravity of the liquid becomes constant, indicating that the potassium carbonate is thoroughly distributed throughout the batch. The excess liquid is then removed by rotating the drum at 370 r.p.m.

The batch is washed with benzene, and the benzene is removed with steam distillation. The product is then washed with water and dried.

The fibrous process has been used for the esterification of wood and cellulose to study the effects of partial substitution. Bletzinger[61] found that rag stock acetylated in the range of 9–25% acetyl with acetic anhydride and pyridine gave a poor paper stock due to the increased water resistance of the fibers. Acetyl values below 6% separate the cellulose molecules and allow greater ease of hydration. Similar work has been done by Stamm[62] who worked with thin layers of wood. Treatment with acetic anhydride–pyridine vapors gave products of about 21% acetyl content having good strength with reduced shrinkage and resistance to decay. Cotton fibers which have been surface acetylated to the extent of about one acetyl group per glucose unit with acetic anhydride and perchloric acid catalyst have outstanding properties.[63]

The strength is about the same as before acetylation, the sensitivity to moisture is less, the heat stability is greatly improved, and there is almost complete protection against attack by microorganisms as long as the acetyl groups are not removed by hydrolysis. X-ray examination shows that the crystalline portions of the fibers are unchanged cellulose.[64]

(c) CELLULOSE PROPIONATE

Cellulose propionate may be prepared by esterification with propionic anhydride in the presence of acid catalysts[65] under conditions similar to those used for cellulose acetate manufacture. The anhydride is somewhat less reactive than acetic anhydride, thus requiring special consideration for the conditions of pretreatment and catalyst concentration.

[61] J. C. Bletzinger, *Ind. Eng. Chem.*, **35**, 474 (1943).

[62] H. Tarkow, A. J. Stamm, and E. C. O. Erickson, U. S. Forest Products Laboratory, Report **1593** (1946).

[63] C. F. Goldthwait, E. M. Buras, and A. S. Cooper, *Textile Research J.*, **21**, 831 (1951).

[64] F. Happey, *J. Soc. Dyers Colourists*, **66**, 14 (1950).

[65] C. Dreyfus and G. Schneider (to Celanese Corp. of America), U. S. Patent 1,824,877 (Sept. 29, 1931); *Chem. Abstracts*, **26**, 305 (1932).

Mild hydrolysis of cellulose tripropionate results in a product soluble in benzene and in butyl acetate. Further hydrolysis of cellulose propionate is reported by Fothergill[66] to give products of particular interest for plastics or film use. The hydrolysis is carried out to give a product of about 47% propionyl content which is insoluble in benzene but soluble in butyl acetate and acetone. Still further hydrolysis results in products insoluble in both benzene and butyl acetate but soluble in acetone, methyl Cellosolve, and dioxane. A particularly good solvent combination for making films and plastics from this cellulose propionate is claimed to be a mixture of 62 parts of acetone, 21 parts of butyl acetate or other nonsolvent component to act as a residual swelling agent, and 17 parts of ethyl alcohol.

Cellulose tripropionate is considerably softer than either the triacetate or its hydrolysis product. Cellulose propionate has been manufactured in limited quantities for use in plastics.

(d) CELLULOSE BUTYRATE

Cellulose butyrate, similarly to the propionate, may be prepared by esterification with the anhydride and a catalyst, such as sulfuric acid, provided the reaction conditions are adjusted to permit an efficient pretreatment and well-controlled esterification. Esselen and Mork[67] in 1922 recommended the use of small quantities of water with butyric acid as a pretreatment step.

Hydrolysis of cellulose tributyrate has been described by Gault and Angla[68] who carried out the reaction in butyric acid of 76–78% strength at a temperature of 45–50°C. Increased hydrolysis results in changes of solubility, the least hydrolyzed materials being soluble in benzene but insoluble in methyl alcohol. Further reaction yields products soluble in both benzene and methyl alcohol and, finally, products soluble in ethyl alcohol but insoluble in benzene.

Herzog and Frank[69] have described a process for the preparation of hydrolyzed cellulose butyrates involving preliminary treatment of cellulose with 87% formic acid at 20°C. This product, which contains a small amount of combined formic acid, is then washed and dried and thereafter esterified with a butyric anhydride—butyric acid mixture and zinc chloride as a catalyst. The reaction product is isolated and then hydrolyzed in 95% butyric acid at 90°C. for 32 hrs. It is soluble in acetone and in mixtures of benzene and alcohol.

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[66] R. E. Fothergill (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,076,555 (Apr. 13, 1937); *Chem. Abstracts,* **31,** 4119 (1937); Brit. Patent 449,182 (June 22, 1936).

[67] G. J. Esselen and H. S. Mork, U. S. Patent 1,425,580 (Aug. 15, 1922); *Chem. Abstracts,* **16,** 3393 (1922).

[68] H. Gault and B. Angla (to Société des usines chimiques Rhône-Poulenc), U. S. Patent 1,912,189 (May 30, 1933); *Chem. Abstracts,* **27,** 4077 (1933); French Patent 685,637 (July 12, 1930); *Chem. Abstracts,* **24,** 6013 (1930).

[69] R. O. Herzog and G. Frank, French Patent 700,165 (Aug. 7, 1930); *Chem. Abstracts,* **25,** 3481 (1931); G. Frank and H. Cohn, *Cellulosechemie,* **12,** 68 (1931).

Cellulose tributyrate melts at a lower temperature than either the acetate or propionate and is considerably softer than those esters. The product has not been made in commercial quantities up to the present time.

(e) MIXED ESTERS OF LOWER ALIPHATIC ACIDS

Cellulose mixed esters containing, in addition to acetyl, either propionyl or butyryl groups offer the opportunity of obtaining products with certain physical properties improved over those of cellulose acetate, at the same time being free from the disadvantages of softness, low strength, and the difficulty of manufacture of cellulose propionate and butyrate.

These mixed esters are commercially manufactured by including the acyl components in the esterification bath in the form of acids or anhydrides. Clarke and Malm[70] have pointed out that acyl groups from propionic or butyric acid may be introduced into a cellulose ester without employing the anhydride if these acids are present in an esterification mixture in which some other active anhydride is present. Propionic acid may in this way be incorporated with acetic anhydride or a mixture of acetic anhydride and acetic acid to produce a uniform product of good quality containing both acyl groups. It is also possible to esterify with propionic or butyric anhydride with acetic acid present in the reaction mixture to produce a mixed ester. The ratio of acetic to propionic or butyric acid obtained in the cellulose derivative will be proportional to the concentration of the corresponding acyl groups in the esterification mixture, making possible accurate control in manufacture (Fig. 20).

It has been found that the relationship shown in Figure 20 exists between the per cent higher acyl of total acyl in the esterification mixture and the per cent higher acyl in the resulting fully esterified cellulose mixed ester. This relationship varies slightly with extreme variations in ratios of esterification mixture to cellulose. For economic reasons it is, of course, better to use as much acetic anhydride and as little higher anhydride as possible; however, for the activation of the cellulose prior to esterification, as much acetic and as little higher acid as possible should be employed to obtain optimum results. The proper proportions of these chemicals must be selected in every case and depend upon the composition and viscosity of the ester to be prepared and the reactivity of the cellulose used.

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[70] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patent 2,048,685 (July 28, 1936).

In the manufacture of cellulose mixed esters, sulfuric acid is the most practical catalyst; however, with increase in the higher acyl content of the esterification mixture, the catalytic efficiency of sulfuric acid decreases because it is less readily sorbed by the cellulose from the esterification mixture.[71] Figure 21 shows the difference in sulfuric acid sorption when cotton linters are kept in a mixture of acetic acid containing 5% acetic anhydride and 0.5% sulfuric acid and in a mixture of butyric acid containing 5% acetic anhydride and 0.5% sulfuric acid. The treatment was carried out at 25°C., with 20 parts of liquid for 1 part of cellulose.

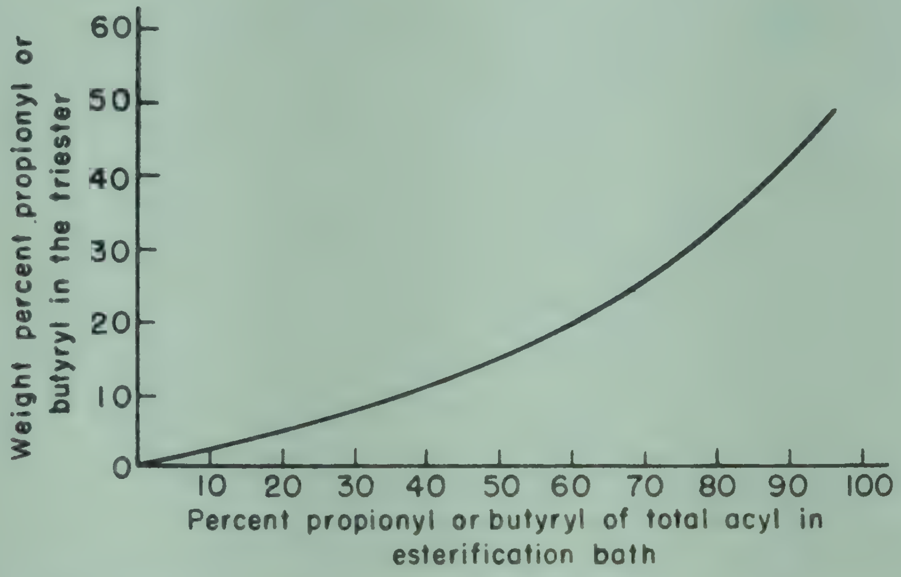

Fig. 20. Relationship between composition of esterification bath and per cent propionyl or butyryl introduced into product.

Butyric and propionic anhydrides react less readily with cellulose than acetic anhydride when sulfuric acid is used as catalyst. The lower sulfuric acid sorption from the higher acids under anhydrous condition and the lower reactivity of the higher anhydrides result in a slower reaction and cause more breakdown of the cellulose before it is protected by acyl groups.

To overcome these handicaps it has been found advisable to decrease the liquid-to-cellulose ratio in the esterification mixture, thereby increasing the anhydride and catalyst concentrations but still keeping their ratio to the cellulose the same. This speeds up the reaction. The cellulose is esterified and protected by acyl groups before it becomes too much degraded, resulting in products of higher viscosity and improved physical properties.[72] Pretreatment is an important step in the preparation of cellulose mixed esters of satisfactory quality and should be so adjusted as to insure uniform esterification and freedom from haze and undissolved fiber in the reaction product.

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[71] C. J. Malm (to Eastman Kodak Co.), U. S. Patent 2,097,954 (Nov. 2, 1937); *Chem. Abstracts*, **32**, 353 (1938); U. S. Patent 2,173,954 (Sept. 26, 1939).

[72] L. W. Blanchard, Jr. (to Eastman Kodak Co.), U. S. Patent 2,208,569 (July 23, 1940); *Chem. Abstracts*, **35**, 316 (1941).

A procedure for preparation of cellulose acetate propionates of high viscosity has been described by Malm.[73] In a process for manufacturing mixed esters containing moderate amounts of butyryl, Billing and Tinsley[74] have recommended pretreatment with acetic acid followed by esterification with butyric acid and acetic anhydride together with a suitable catalyst.

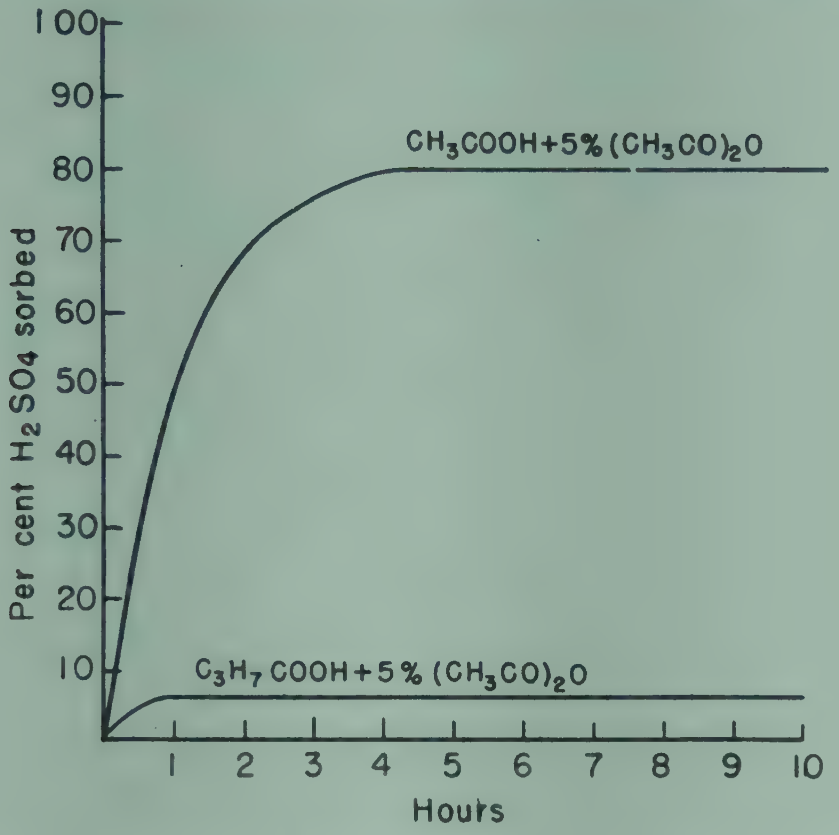

Fig. 21. Sorption of sulfuric acid by cotton linters in the presence of acetic and butyric acids.

Mixed esters containing very high proportions of propionyl or butyryl groups require special procedures for their manufacture. Gardner[75] has described a method calling for from 5–20% water, based upon the weight of the cellulose, in pretreatment mixtures in which acids of three to four carbon atoms predominate. The presence of this amount of moisture is very effective in bringing about a uniform esterification reaction.

The hydrolysis of fully esterified mixed esters containing at least 15% propionyl or butyryl groups has been reported by Malm and Fletcher[76] to bring about changes in solubility and physical properties which make the products more useful than the unhydrolyzed esters.

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[73] C. J. Malm (to Eastman Kodak Co.), U. S. Patent 2,026,986 (Jan. 7, 1936); *Chem. Abstracts*, **30**, 1559 (1936).

[74] W. M. Billing and J. S. Tinsley (to Hercules Powder Co.), U. S. Patent 1,973,693 (Sept. 18, 1934); *Chem. Abstracts*, **28**, 7013 (1934).

[75] H. S. Gardner, Jr. (to Eastman Kodak Co.), U. S. Patent 2,113,301 (Apr. 5, 1938); *Chem. Abstracts*, **32**, 4335 (1938).

[76] C. J. Malm and C. L. Fletcher (to Eastman Kodak Co.), U. S. Patent 2,026,583 (Jan. 7, 1936); *Chem. Abstracts*, **30**, 1230 (1936).

(f) HIGHER ALIPHATIC ACID ESTERS

Anhydrides of organic acids containing more than four carbon atoms cannot readily be made to esterify cellulose by use of acid catalysts, and these esters therefore require other methods of preparation. Grün and Wittka[77] treated cellulose with lauryl and stearyl chlorides in pyridine at "the temperature of a water bath," and obtained partially esterified products which were not changed in appearance from the original cellulose. Gault and Ehrmann[78] described the preparation of several cellulose higher esters using benzene as a diluent for the pyridine and acid chloride reaction. Mono-, di-, and tri-esters of lauric, palmitic, and stearic acids were made. Products from unmodified cellulose were found to be insoluble; modified cellulose, such as that regenerated from viscose or cuprammonium solution, gave soluble esters. The use of benzene or toluene as a diluent for the pyridine–acid chloride reaction mixture offers a considerable improvement in operation, the hydrocarbon acting at elevated temperatures as a solvent for the intermediate product between the acid chloride and the tertiary base. A still better diluent for this purpose is chlorobenzene, which has been used by Hagedorn.[79]

Kita and others[80] have shown that alkali cellulose reacts with higher acid chlorides to give degrees of substitution varying with alkali concentration. Sakurada and Nakashima,[81] by repeated treatment with alkali and stearyl chloride, obtained a degree of substitution of 2.1.

Clarke and Malm[3] used chloroacetic anhydride as an impelling agent to bring about the esterification of cellulose with higher acids. A series of esters from the acetate through the stearate was prepared and the properties studied.

Malm and coworkers[82] used the acid chloride–pyridine method to pre-

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[77] A. Grün and F. Wittka, *Z. angew. Chem.*, **34,** 645 (1921).

[78] H. Gault and P. Ehrmann, *Compt. rend.*, **177,** 124 (1923); *Chimie & industrie*, Special No. 574 (May, 1924); *Bull. soc. chim.*, [4], **39,** 873 (1926).

[79] M. Hagedorn and O. Reichert (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,832,381 (Nov. 17, 1931); *Chem. Abstracts*, **26,** 1438 (1932); M. Hagedorn and G. Hingst (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,940,589 (Dec. 19, 1933); *Chem. Abstracts*, **28,** 1532 (1934).

[80] G. Kita, I. Sakurada, and T. Nakashima, *Cellulose Ind.* (Tokyo), **2,** 30 (1926); J. Leibowitz, *Cellulosechemie*, **9,** 125 (1928).

[81] I. Sakurada and T. Nakashima, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **6,** 197 (1927).

[82] C. J. Malm, J. W. Mench, D. L. Kendall, and G. D. Hiatt, *Ind. Eng. Chem.*, **43,** 684 (1951).

TABLE 9

Summary of the Properties of Cellulose Triesters. (Malm, Mench, Kendall, and Hiatt[82])

Ester	C Atoms	Behavior on heating			Water tolerance value[a]	% Moisture regain				Density, g./ml.	Tensile strength, kg./mm.²
		Shrinking point, °C.	Melting point, °C.	Char point, °C.		25% R.H.	50% R.H.	75% R.H.	95% R.H.		
Cellulose[b]	0	—	—	—	—	5.4	10.8	15.5	30.5	1.52	—
Acetate	2	—	306	315	54.4	0.6	2.0	3.8	7.8	1.28	7.3
Propionate	3	229	234	> 315	26.9	0.1	0.5	1.5	2.4	1.23	4.9
Butyrate	4	178	183	> 315	16.1	0.1	0.2	0.7	1.0	1.17	3.1
Valerate	5	119	122	> 315	10.2	0	0.2	0.3	0.6	1.13	1.9
Caproate	6	84	94	> 315	5.88	0	0.1	0.2	0.4	1.10	1.4
Heptylate	7	82	88	290	3.39	0	0.1	0.2	0.4	1.07	1.1
Caprylate	8	82	86	315	1.14	0	0.1	0.1	0.2	1.05	0.9
Caprate	10	87	88	310	—	0	0.1	0.2	0.5	1.02	0.7
Laurate	12	89	91	> 315	—	0	0.1	0.1	0.3	1.00	0.6
Myristate	14	87	106	315	—	0	0.1	0.1	0.2	0.99	0.6
Palmitate	16	90	105	315	—	0	0.1	0.1	0.2	0.99	0.5

[a] Milliliters of water required to start precipitation of ester from 125 ml. of an acetone solution of 0.1% concentration.

[b] Starting cellulose, prepared by deacetylation of commercial, medium-viscosity cellulose acetate (40.4% acetyl content).

pare a series of fully esterified esters, essentially free from contaminating groups and with each member of the series having as nearly as possible the same degree of polymerization. A cellulose regenerated from a commercial cellulose acetate served as the starting material. Reaction conditions were studied to find the best ratio of acid chloride to pyridine and the preferred time, temperature, and reaction diluent. Esters were put through the reaction a second time and checked by analysis for complete esterification. Portions of the finished esters were de-esterified and the recovered celluloses found to have similar intrinsic viscosities in cuprammonium solution. A summary of the properties of these esters is given in Table 9.

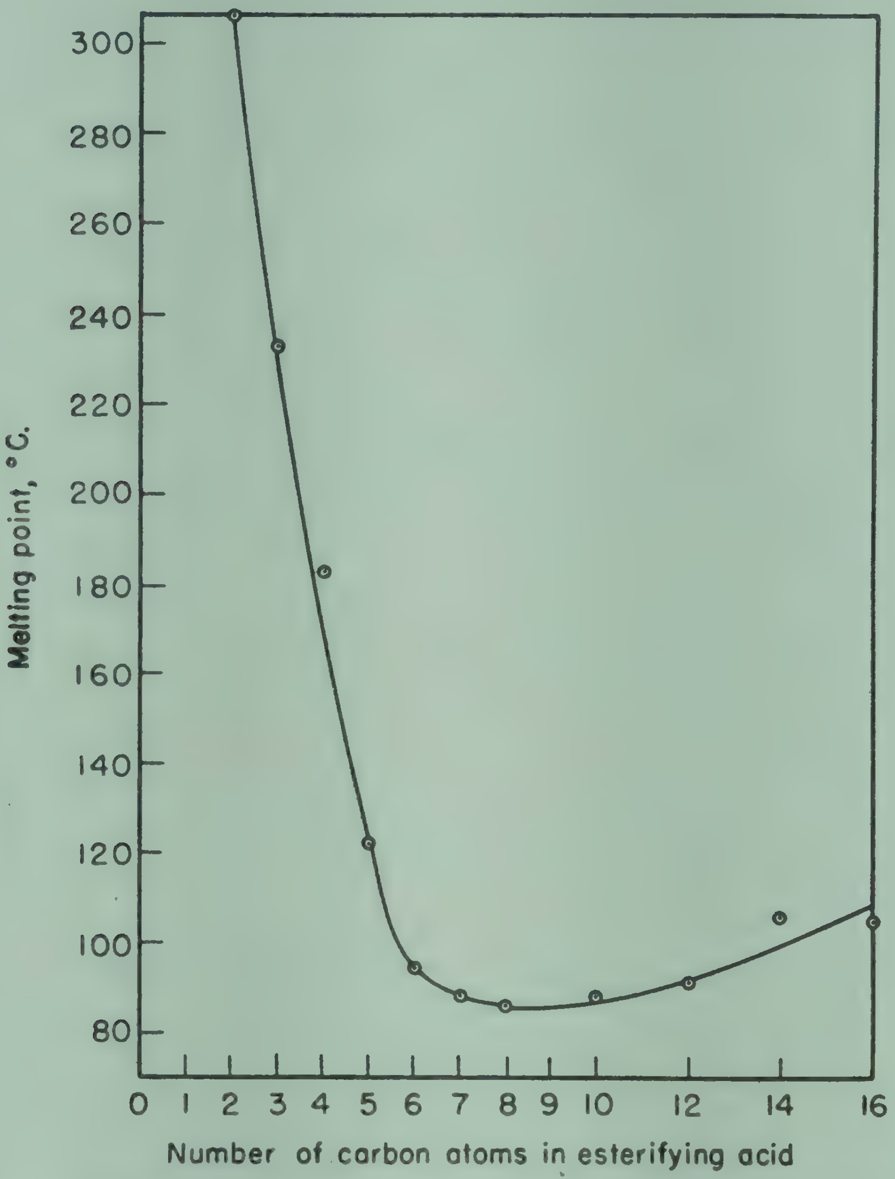

Fig. 22. Melting points of triesters (Malm, Mench, Kendall, and Hiatt[82]).

Melting points were found to fall off sharply, then rise toward the end of the series, as shown in Figure 22.

Water tolerance values, a photometric measure of the amount of water required to produce a given level of haze in a dilute solution of the ester in

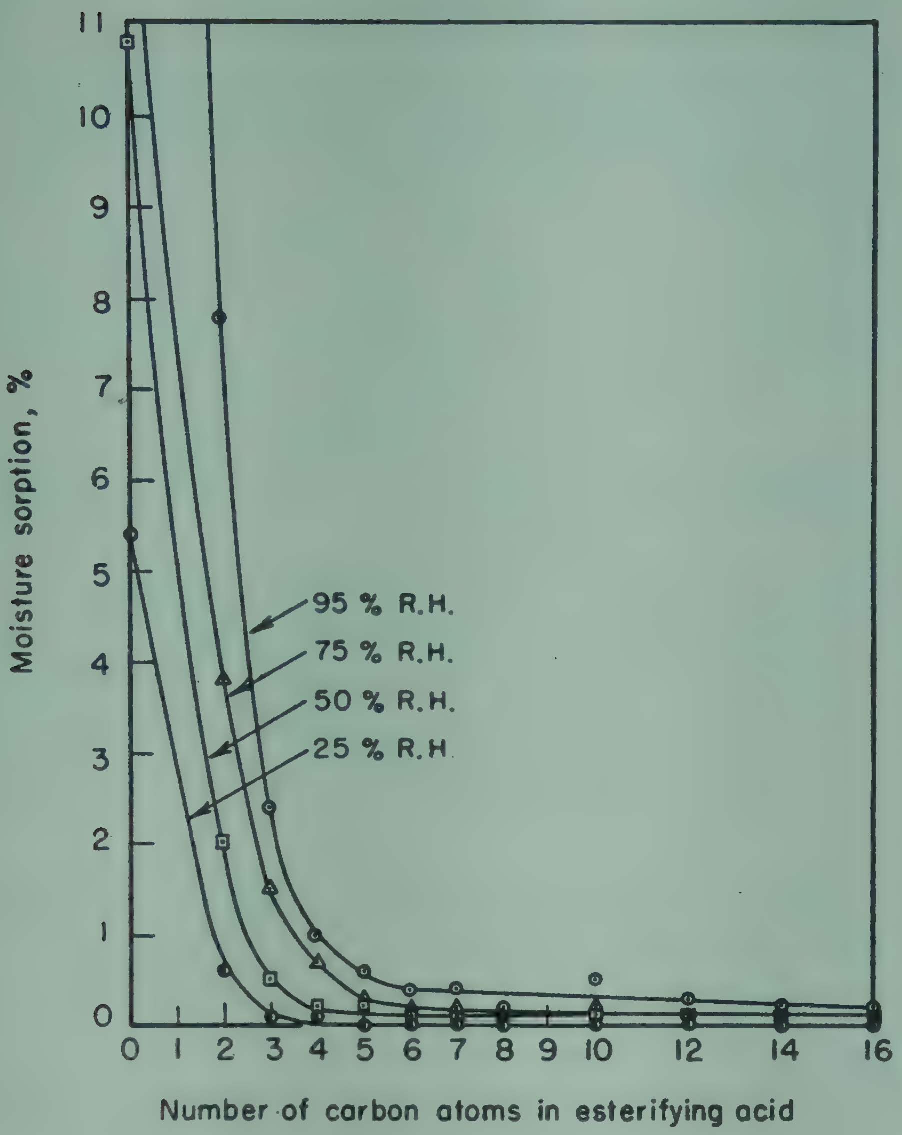

Fig. 23. Per cent moisture sorption of triesters at 25°C. (Malm, Mench, Kendall, and Hiatt[82]). See text p. 796.

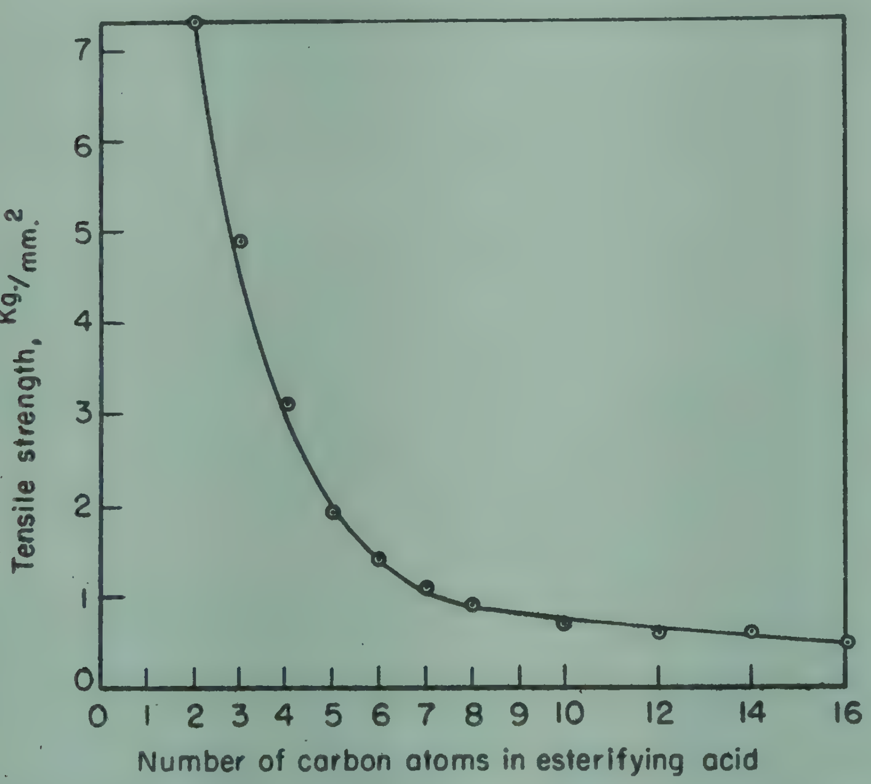

Fig. 24. Tensile strengths of triesters (Malm, Mench, Kendall, and Hiatt[82]). See text p. 796.

TABLE 10

Solubilities of the Cellulose Triesters of the *n*-Fatty Acids
(Malm, Mench, Kendall, and Hiatt[82])
Solvent-solid ratio 9:1 by weight. See text p. 796.

		Cellulose Triester											
		Acetate	Propionate	Butyrate	Valerate	Caproate	Heptylate	Caprylate	Caprate	Laurate	Myristate	Palmitate	
	SOLVENT / C Atoms in Acid	2	3	4	5	6	7	8	10	12	14	16	
	Alcohols												
1	Methanol				▨								1
2	Ethanol			▨	▨	▨							2
3	i-Propanol			▨	▨	■	■	■	▨				3
4	n-Butanol			▨	▨	■	■	■	■	▨	▨	▨	4
5	t-Butanol			▨	■	■	■	■	■	▨	▨	▨	5
6	2-Ethylhexanol				▨	■	■	■	■	▨	▨	▨	6
7	Diacetone Alcohol		▨	■	■	■	■	▨					7
8	Tetrahydrofurfuryl Alcohol		■	■	■	■	▨						8
	Ether-Alcohols												
9	β-Methoxyethanol		▨	▨	▨	▨							9
10	β-Ethoxyethanol		▨	▨	■	■	■	▨					10
11	β-Butoxyethanol		▨	▨	■	■	■	■	▨				11
12	Ethyl Carbitol												12
13	Butyl Carbitol			▨	▨	■	■	■	▨				13
	Ethers and Acetals												
14	Ethyl Ether				■	■	■	■	■	■	■	▨	14
15	Isopropyl Ether				▨	■	■	■	■	■	■	▨	15
16	Diethyl Cellosolve		▨	■	■	■	■	■					16
17	1,4-Dioxane		■	■	■	■	■	■	■	▨	▨	▨	17
18	Tetrahydrofuran		■	■	■	■	■	■	■	■	■	■	18
19	Ethylene Formal		■	■	■	■	■	■	■				19
	Ketones												
20	Acetone		■	■	■	■	■	■					20
21	Methyl Ethyl Ketone		■	■	■	■	■	■	■	■	▨	▨	21
22	Methyl Isobutyl Ketone		■	■	■	■	■	■	■	■	▨	▨	22
23	Cyclohexanone		■	■	■	■	■	■	■	■	■	▨	23
24	Isophorone		■	■	■	■	■	■	■	■	▨	▨	24
	Esters												
25	Methyl Formate		■	■	■	■							25
26	Methyl Acetate		■	■	■	■	■	■	▨				26
27	Ethyl Acetate		■	■	■	■	■	■	■	■	▨	▨	27
28	Isopropyl Acetate		■	■	■	■	■	■	■	■	▨	▨	28
29	n-Butyl Acetate		■	■	■	■	■	■	■	■	▨	▨	29
30	n-Amyl Acetate		■	■	■	■	■	■	■	■	▨	▨	30
31	β-Methoxyethyl Acetate		■	■	■	■	■	▨					31
32	β-Ethoxyethyl Acetate		■	■	■	■	■	■	▨				32
33	Ethyl Lactate		▨	■	■	▨	▨						33
34	β-Hydroxyethyl Acetate		▨	▨									34
	Halogenated Compounds												
35	Methylene Chloride	■	■	■	■	■	■	■	■	■	■	■	35
36	Ethylene Chloride		■	■	■	■	■	■	■	■	■	▨	36
37	Propylene Chloride		■	■	■	■	■	■	■	■	■	▨	37
38	Chloroform	■	■	■	■	■	■	■	■	■	■	■	38
39	Carbon Tetrachloride			■	■	■	■	■	■	■	■	■	39
40	Trichloroethylene		■	■	■	■	■	■	■	■	■	■	40
41	s-Tetrachloroethane	■	■	■	■	■	■	■	■	■	■	■	41
42	n-Amyl Chloride			■	■	■	■	■	■	■	■	■	42
43	Chlorobenzene		■	■	■	■	■	■	■	■	■	■	43
44	Fluorobenzene		■	■	■	■	■	■	■	■	■	■	44
45	Ethylene Chlorohydrin	▨	■	■	■	■							45
46	β,β'-Dichloroethyl Ether		■	■	■	■	■	■	▨				46

TABLE 10 (*Continued*)

		Cellulose Triester											
		Acetate	Propionate	Butyrate	Valerate	Caproate	Heptylate	Caprylate	Caprate	Laurate	Myristate	Palmitate	
	C Atoms in Acid	2	3	4	5	6	7	8	10	12	14	16	
	Nitrogen Compounds												
47	Pyridine	□	■	■	■	■	■	■	■	▨	▨	▨	47
48	Morpholine	▨	■	■	■	■	■	■	□	□	□	□	48
49	Formamide	□	□	□	□	□	□	□	□	□	□	□	49
50	Acrylonitrile	□	■	■	■	■	■	■	□	□	□	□	50
51	Nitromethane	▨	■	■	▨	□	□	□	□	□	□	□	51
52	Nitroethane	□	■	■	■	■	▨	▨	□	□	□	□	52
53	2-Nitropropane	□	■	■	■	■	■	■	■	□	□	□	53
54	Nitrobenzene	□	■	■	■	■	■	■	▨	□	□	□	54
	Acids												
55	Formic Acid	■	■	▨	□	□	□	□	□	□	□	□	55
56	Acetic Acid	□	■	■	■	▨	□	□	□	□	□	□	56
	Hydrocarbons												
57	n-Hexane	□	□	□	▨	■	■	■	■	■	■	▨	57
58	Cyclohexane	□	□	□	▨	■	■	■	■	■	■	▨	58
59	Benzene	□	■	■	■	■	■	■	■	■	■	■	59
60	Toluene	□	▨	▨	■	■	■	■	■	■	■	■	60
61	Xylene	□	□	▨	▨	■	■	■	■	■	■	■	61
62	Solvent Naphtha #3	□	□	□	▨	■	■	■	■	■	■	▨	62
63	V. M. & P. Naphtha	□	□	□	▨	■	■	■	■	■	■	▨	63
64	Turpentine	□	□	□	▨	■	■	■	■	■	■	▨	64
	Mixtures												
65	Acetone:Water (4:1)	□	▨	□	□	□	□	□	□	□	□	□	65
66	Acetone:Methanol(4:1)	□	■	■	■	■	■	□	□	□	□	□	66
67	" " (1:1)	□	■	■	■	■	□	□	□	□	□	□	67
68	" " (1:4)	□	□	▨	▨	□	□	□	□	□	□	□	68
69	Ethyl Acetate:Ethanol(4:1)	□	■	■	■	■	■	■	▨	□	□	□	69
70	" " (1:1)	□	▨	■	■	■	▨	□	□	□	□	□	70
71	Methylene Chloride:Methanol(4:1)	■	■	■	■	■	■	■	□	□	□	□	71
72	" " " (1:1)	□	■	■	■	□	□	□	□	□	□	□	72
73	" " " (1:4)	□	□	▨	▨	□	□	□	□	□	□	□	73
74	Ethylene Chloride:Methanol(4:1)	▨	■	■	■	■	■	■	▨	□	□	□	74
75	" " " (1:1)	□	■	■	■	▨	▨	□	□	□	□	□	75
76	" " " (1:4)	□	□	▨	▨	□	□	□	□	□	□	□	76
77	Propylene Chloride:Methanol(4:1)	□	■	■	■	■	■	■	■	■	▨	▨	77
78	" " " (1:1)	□	■	■	■	■	▨	□	□	□	□	□	78
79	" " " (1:4)	□	□	▨	▨	□	□	□	□	□	□	□	79
80	Nitroethane:Ethanol(4:1)	□	■	■	■	■	■	▨	□	□	□	□	80
81	Acetic Acid:Water(4:1)	□	▨	□	□	□	□	□	□	□	□	□	81
82	Benzene:Methanol(4:1)	□	■	■	■	■	■	■	■	■	■	■	82
83	" " (1:1)	□	■	■	■	▨	□	□	□	□	□	□	83
84	" " (1:4)	□	□	▨	■	□	□	□	□	□	□	□	84
85	Toluene:Methanol(4:1)	□	■	■	■	■	■	■	■	■	■	■	85
86	" " (1:1)	□	■	■	■	▨	□	□	□	□	□	□	86
87	" " (1:4)	□	□	▨	▨	□	□	□	□	□	□	□	87
88	β,β'-Dichloroethyl Ether:Methanol (4:1)	□	■	■	■	■	■	▨	□	□	□	□	88
		2	3	4	5	6	7	8	10	12	14	16	

Key:

■ Grain-free solution at 25°C.
▨ Grainy or swollen at 25°C.; grain-free at 100°C. or at B.P. of solvent.
□ Insoluble at 25°C. and at 100°C. or at B.P. of solvent.

acetone, became extremely low for the high esters. Likewise, the moisture sorption values at different relative humidities fell rapidly and were well below 1% for most of the esters (see Fig. 23, p. 793).

Tensile strength measurements on films cast from chloroform solutions fell regularly and then levelled off roughly between C_7 and C_{16}, as shown in Figure 24 (p. 793).

Solubilities were determined in 88 different solvents and mixtures shown in Table 10. The most widely soluble esters were the valerate and caproate. The chlorinated solvents methylene chloride, chloroform, and *s*-tetrachloroethane were the only compounds tested which were solvents throughout the entire series.

Bartell and Ray[82a,82b] measured the contact angles of water and various organic solvents on several simple and mixed cellulose esters. From these measurements an order of hydrophobicity was established for esters with various substituent groups.

Cellulose mixed higher esters, particularly those containing a substantial amount of acetyl and a higher molecular weight acid, have very interesting properties. These mixed esters may be readily prepared, for example, from acetone-soluble cellulose acetate by esterification of the free hydroxyl groups with the desired high molecular weight acid. This may be accomplished either by heating a pyridine solution of the cellulose acetate with a large excess of the higher acid chloride[83] or by the use of chloroacetic anhydride and the higher acid. The resulting products show a wide range of solubility in ketones, esters, and mixtures of toluene with alcohol. They are highly compatible with a large variety of resins, fats, and oils. The products are highly resistant to sorption of moisture.

Cellulose esters of naphthenic acids have been prepared by Kita, Mazume, Sakrada, and Nakashima[84] by a variety of reaction processes. Anhydrides gave only low degrees of esterification; acid chlorides yielded products between the di- and tri-esters. Complete esterification was not obtained. Patents have described the action of naphthenic acid chlorides upon cellulose in the presence of picoline and chlorobenzene at a temperature of 135°C.[85] Mixed esters have also been prepared by treatment of alkali cellulose[86] with mixtures of aliphatic and naphthenic acid chlorides or by

[82a] F. E. Bartell and B. R. Ray, *J. Am. Chem. Soc.*, **74**, 778 (1952).

[82b] B. R. Ray and F. E. Bartell, *J. Phys. Chem.*, **57**, 49 (1953).

[83] H. Gault and P. Ehrmann, *Caoutchouc & gutta-percha*, **24**, 13748, 13824 (1927).

[84] G. Kita, T. Mazume, J. Sakrada, and T. Nakashima, *Kunststoffe*, **16**, 167 (1926).

[85] I. G. Farbenindustrie Akt.-Ges., Brit. Patent 305,947 (June 11, 1930).

[86] M. Hagedorn (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,994,608 (Mar. 19, 1935); *Chem. Abstracts*, **29**, 3157 (1935).

esterification of cellulose with these chlorides in the presence of a tertiary base.[87]

(g) USES OF ALIPHATIC FATTY ACID ESTERS

Since the physical properties of cellulose esters determine their end uses, an understanding of property trends is desirable. The commercially available cellulose esters include cellulose acetates of several acetyl levels and a few acetate butyrate esters covering a wide composition range. Propionate and acetate propionate esters will not be considered, since their properties lie between those of the acetates and the acetate butyrates, and accordingly can be duplicated by proper choice from these groups.

An attempt has been made in Figure 25 to summarize the property trends in the acetates and acetate butyrates between the tri- and di-ester composition lines. Commercial acetates are available in the 38–44% (*a*–*b*) acetyl range. The small letters *c*, *d*, *e*, and *f* locate commercially available mixed esters containing acetyl and with butyryl levels at 16, 27, 38, and 48%, respectively. Tensile strength and stiffness are highest with the simple acetates; flexibility improves with introduction of the higher acyl group. Moisture sorption is lowest with high degrees of butyryl substitution and with fully esterified products, the uptake increasing with relative humidity and the hydroxyl content of the ester, as shown in Figure 26a and 26b.[88]

The simple acetates are higher melting than the mixed esters. With any given triester the melting point drops, then rises again with continued hydrolysis (see Fig. 27).

Hydrolysis of the simple and mixed triesters improves solubility in polar solvents or mixtures containing polar solvents and reduces solubility in, and tolerance for, nonpolar solvents. The behavior of polar solvents is shown by β-methoxyethyl alcohol and by a 1:1 mixture of toluene:methanol, while nonpolar solvents are represented by propylene chloride and methyl isobutyl ketone. Increase in the butyryl content of an ester improves solubility (Figs. 28a, 28b, 28c, and 28d).

The same considerations affecting solvent solubility hold true for plasticizer solubility but to a lesser degree. This is shown in Figure 29a, 29b, and 29c by improved solubility in ethyl phthalate and tripropionin as the ester is hydrolyzed. Solubilities in octyl phthalate show the influence of high butyryl content.

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[87] M. Hagedorn and P. Möller (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,975,897 (Oct. 9, 1934); *Chem. Abstracts*, **28**, 7528 (1934).

[88] C. J. Malm, C. R. Fordyce, and H. A. Tanner, *Ind. Eng. Chem.*, **34**, 430 (1942).

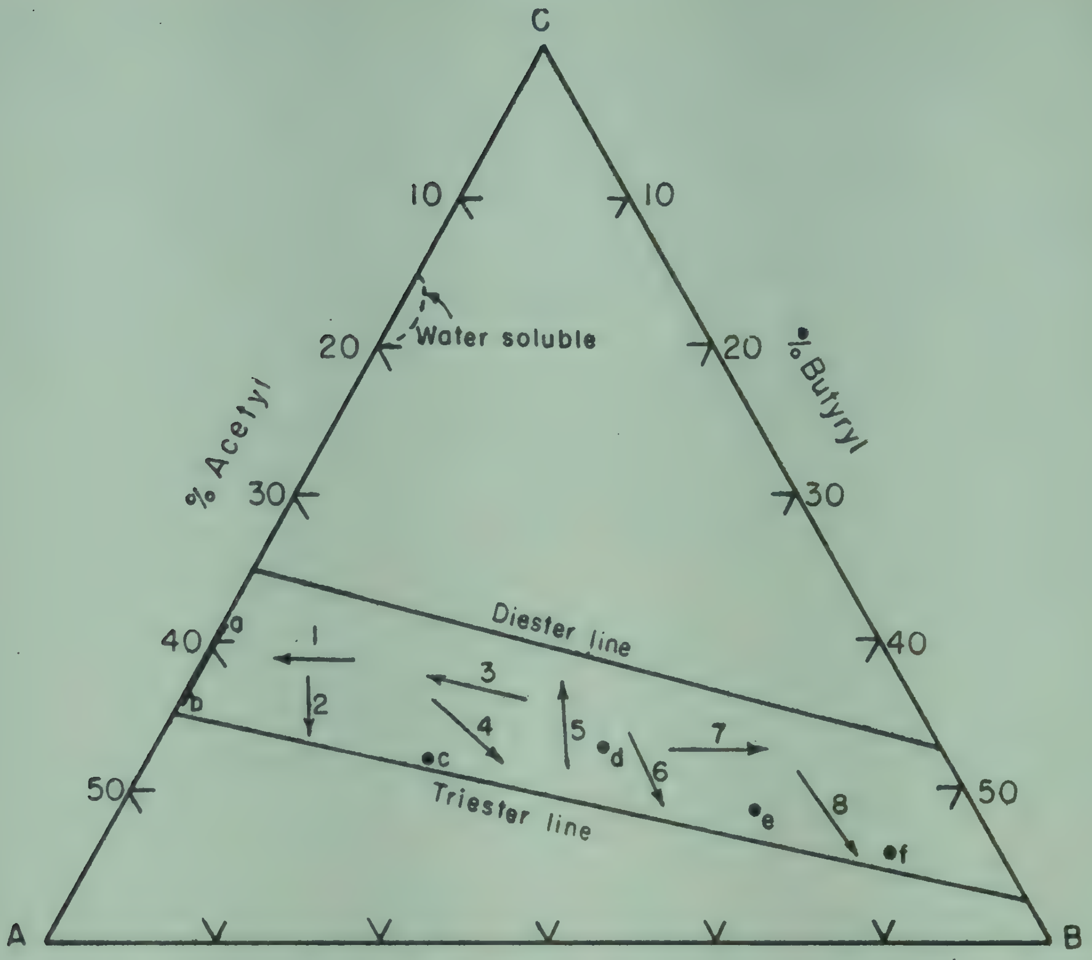
C
10
10
Water soluble
20
20
% Acetyl
% Butyryl
30
30
Diester line
40
40
a
1
b
3
2
4
5
d
6
7
c
50
Triester line
e
8
f
50
A
B

Fig. 25. Effects of composition on physical properties. Apices: A = acetyl; B = butyryl; C = cellulose. 1, increased tensile strength, stiffness; 2, decreased moisture sorption; 3, increased melting point; 4, increased plasticizer compatibility; 5, increased solubilities in polar solvents; 6, increased solubilities in nonpolar solvents; 7, increased flexibility; 8, decreased density.

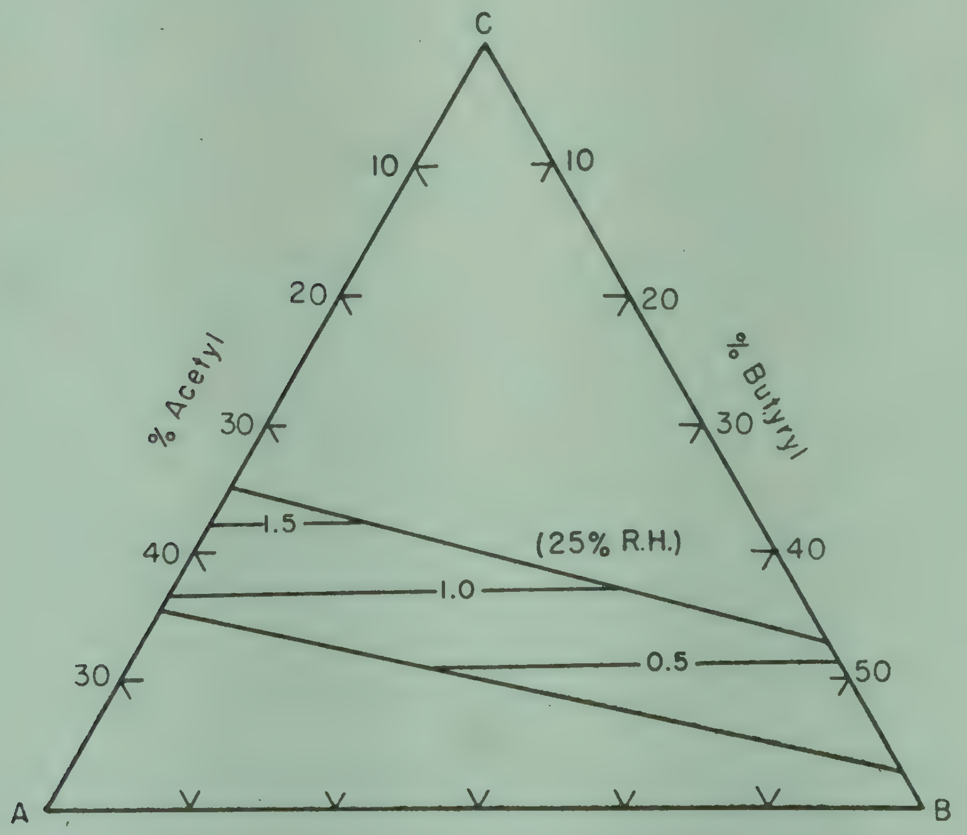

Fig. 26a. Per cent sorption of moisture by cellulose esters of acetic acid at 25% relative humidity (Malm, Fordyce, and Tanner[88]).

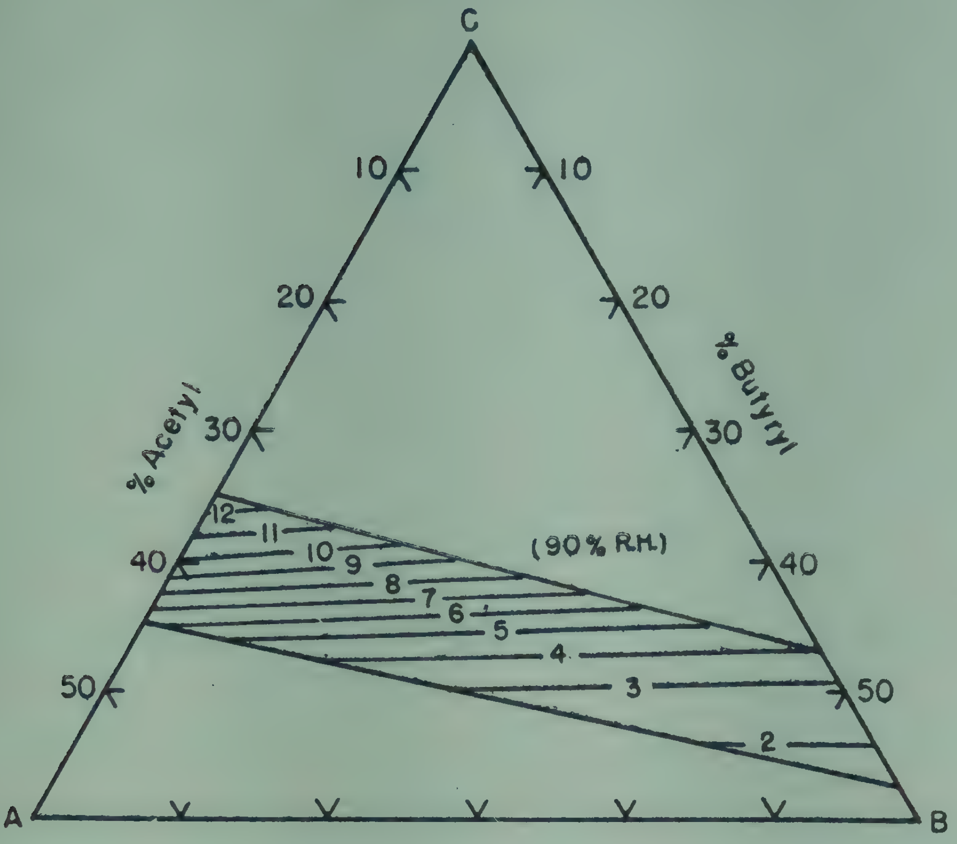

Fig. 26b. Per cent sorption of moisture by cellulose esters of acetic acid at 90% relative humidity (Malm, Fordyce, and Tanner[88]).

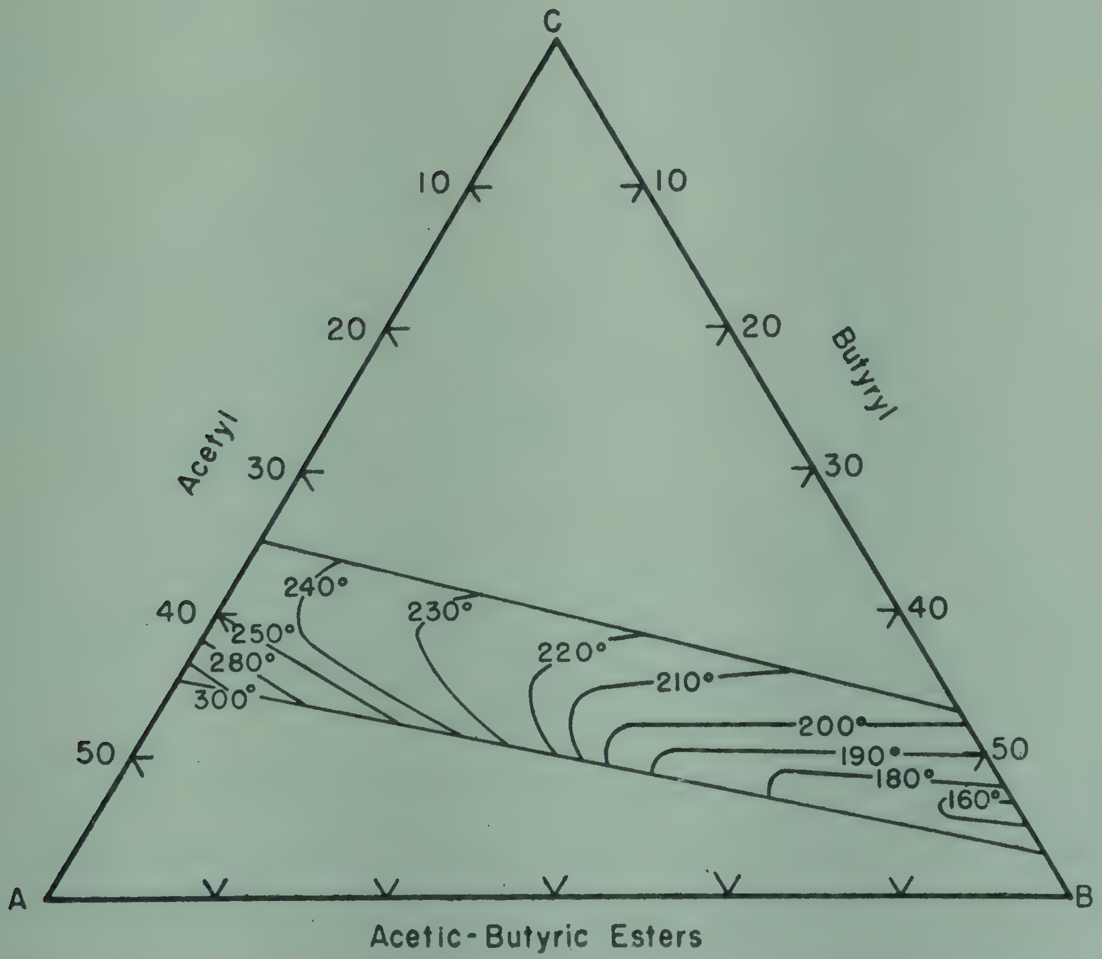

Fig. 27. Relation of composition of cellulose esters of acetic and butyric acids to melting point in °C. (Malm, Fordyce, and Tanner[88]).

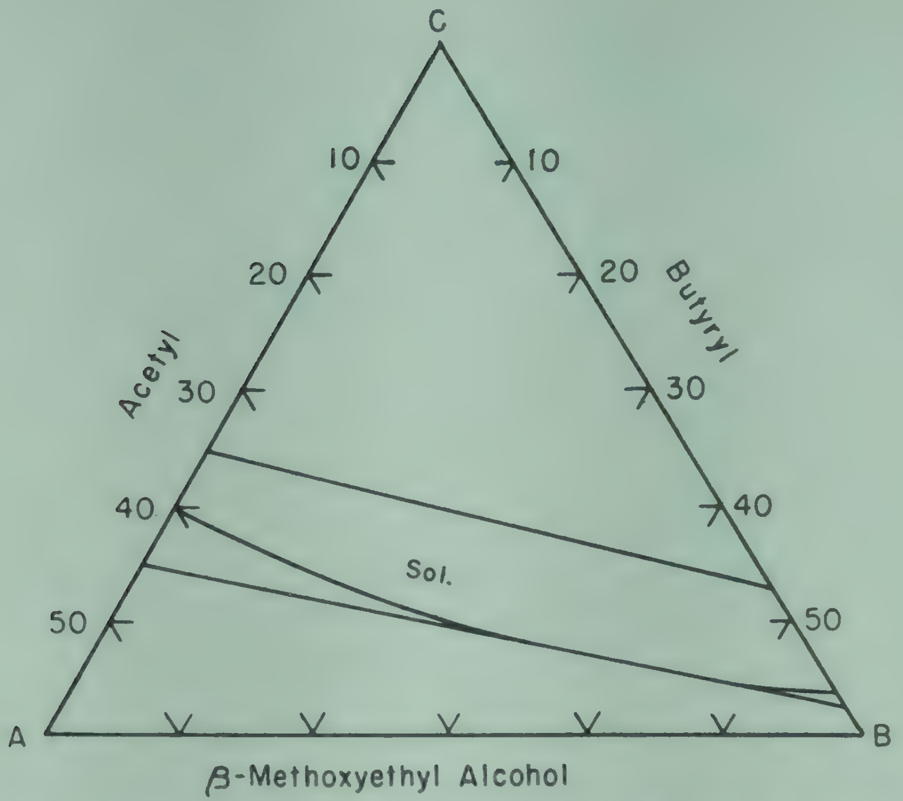

Fig. 28a. Relation of solubility in β-methoxyethyl alcohol to degree of hydrolysis (Malm, Fordyce, and Tanner[88]).

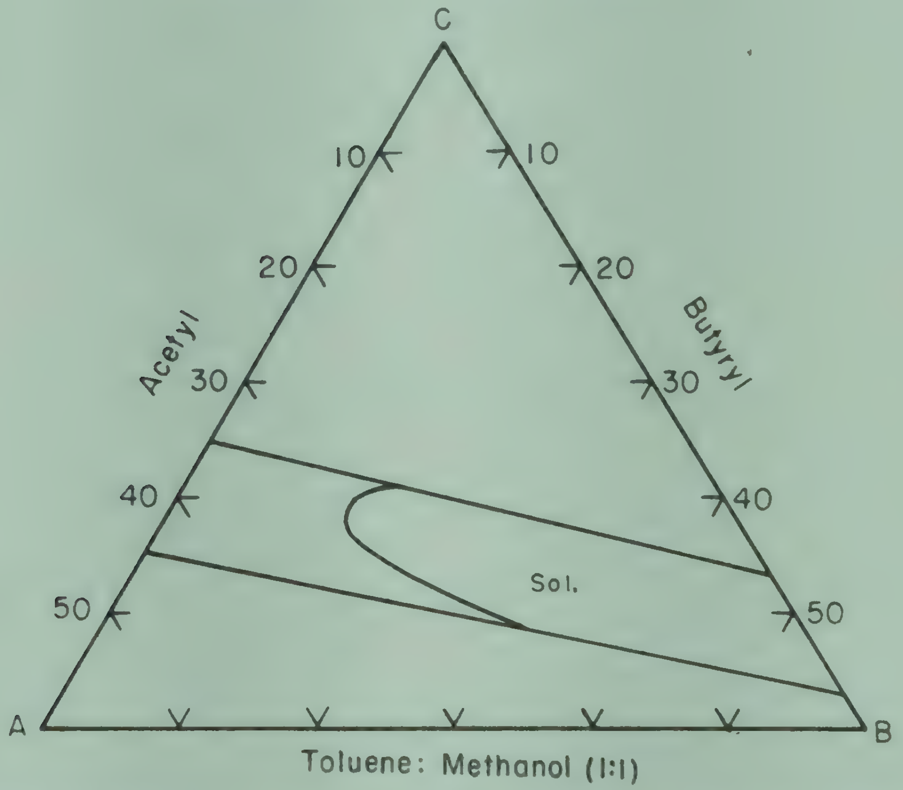

Fig. 28b. Relation of solubility in toluene:methanol (1:1) to degree of hydrolysis (Malm, Fordyce, and Tanner[88]).

Cellulose ester density decreases as the amount of butyryl is increased in the mixed esters as shown in Figure 30.

The foregoing general property trends help to explain the uses and limitations in applications of the cellulose esters.

Cellulose triacetate, the first of the acetates made, has only recently become of commercial importance. Its limited solvent solubility has

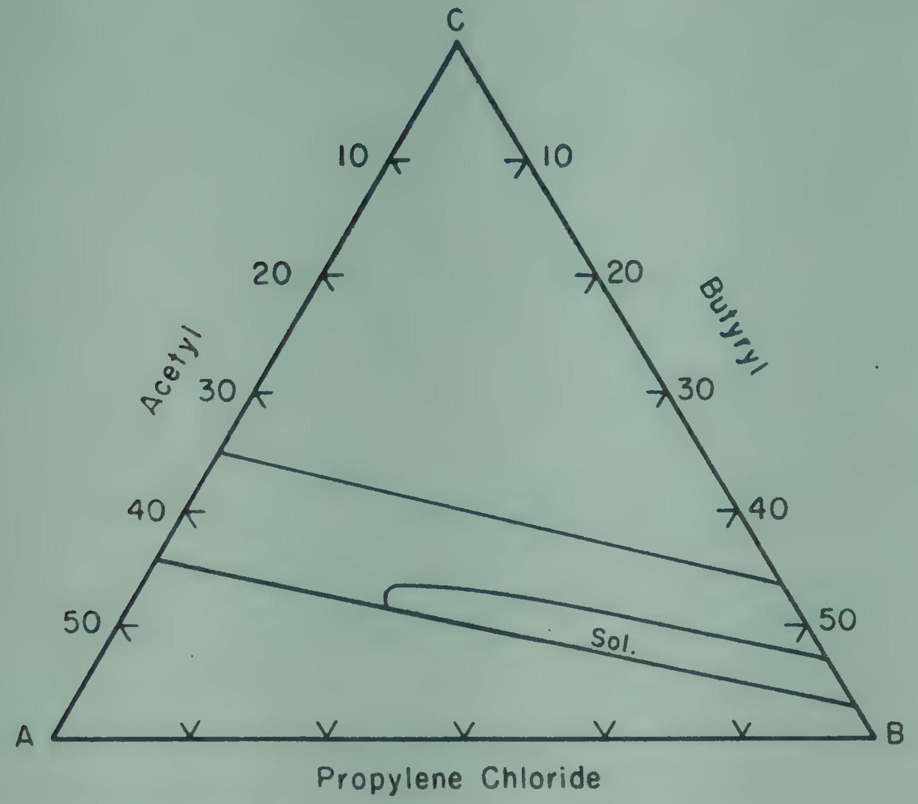

Fig. 28c. Relation of solubility in propylene chloride to degree of hydrolysis (Malm, Fordyce, and Tanner[88]).

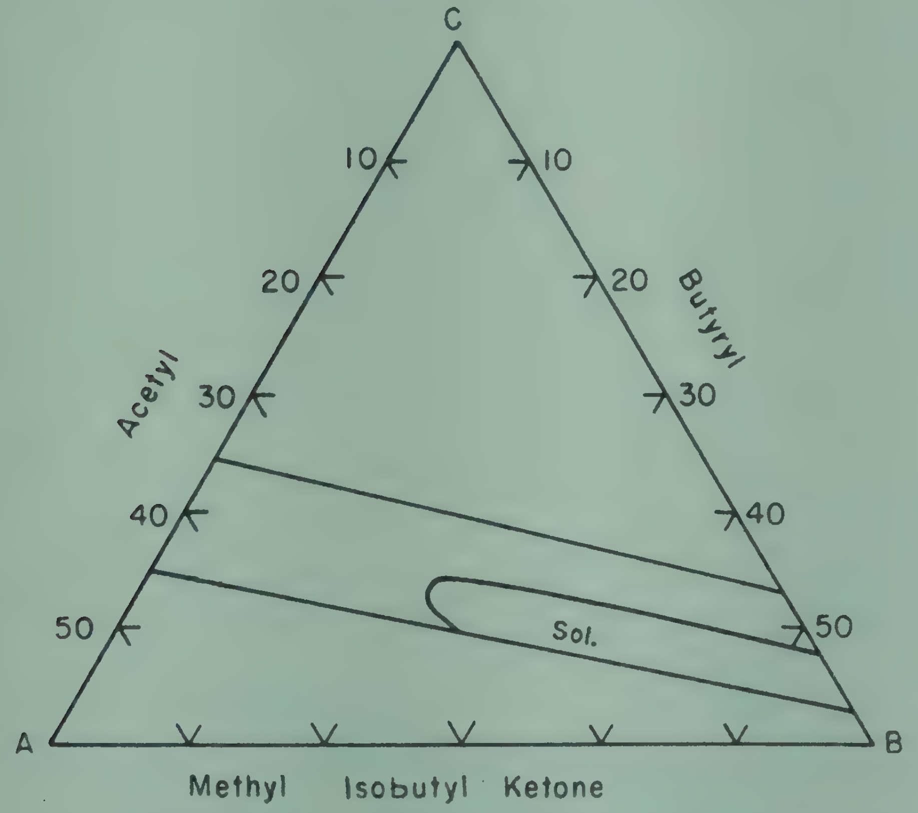

Fig. 28d. Relation of solubility in methyl isobutyl ketone to degree of hydrolysis (Malm, Fordyce, and Tanner[88]).

restricted its use; most emphasis has been placed on the hydrolyzed acetates in the acetone-soluble range. Because it has a higher melting point and better moisture resistance than hydrolyzed acetates, "triacetate" has found a place in the photographic industry in replacing cellulose nitrate as a Ciné film base. (The "triacetate" in use is 1–2% lower in acetyl content than the 44.8% acetyl of the triacetate but is still considerably removed

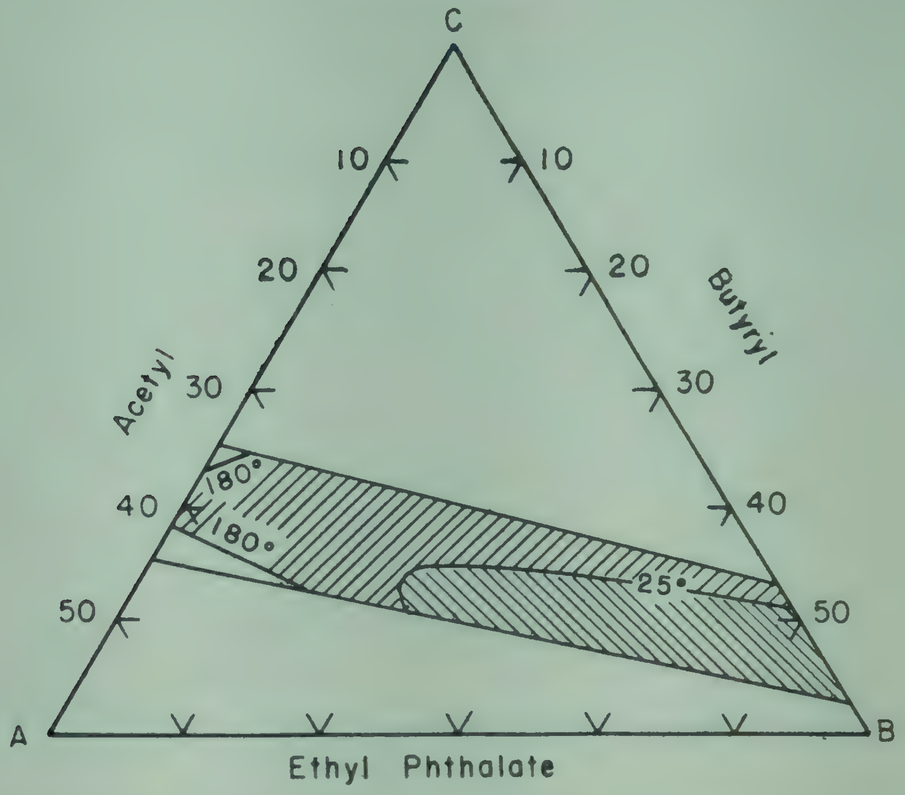

Fig. 29a. Relation of cellulose ester composition to solubility in ethyl phthalate at 25° and 180 °C. (Malm, Fordyce, and Tanner[38]).

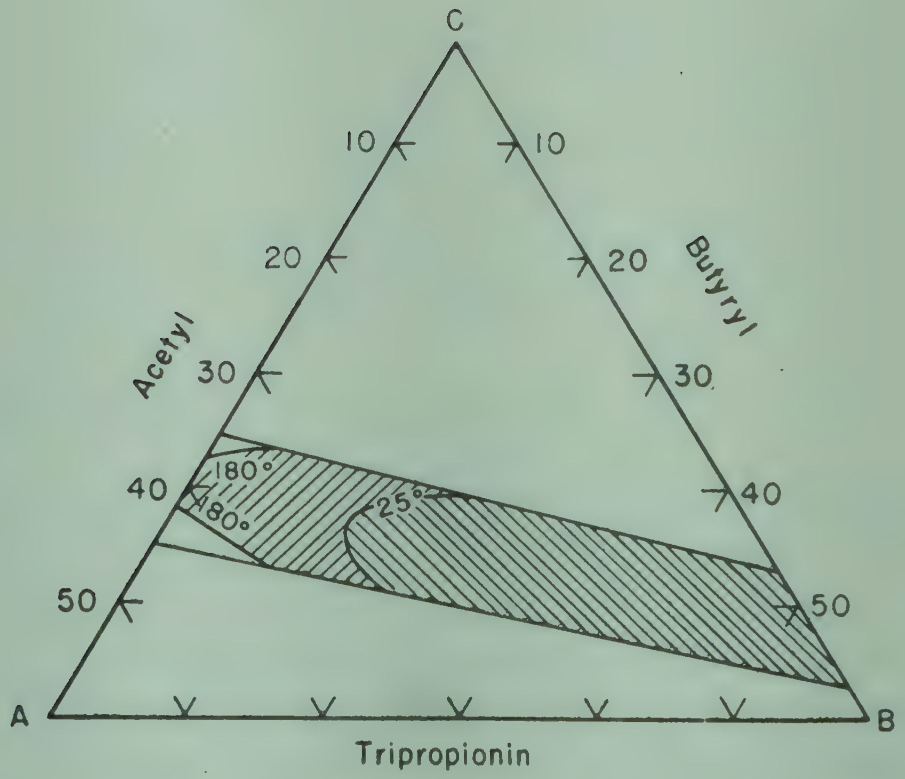

Fig. 29b. Relation of cellulose ester composition to solubility in tripropionin at 25° and 180 °C. (Malm, Fordyce, and Tanner[38])

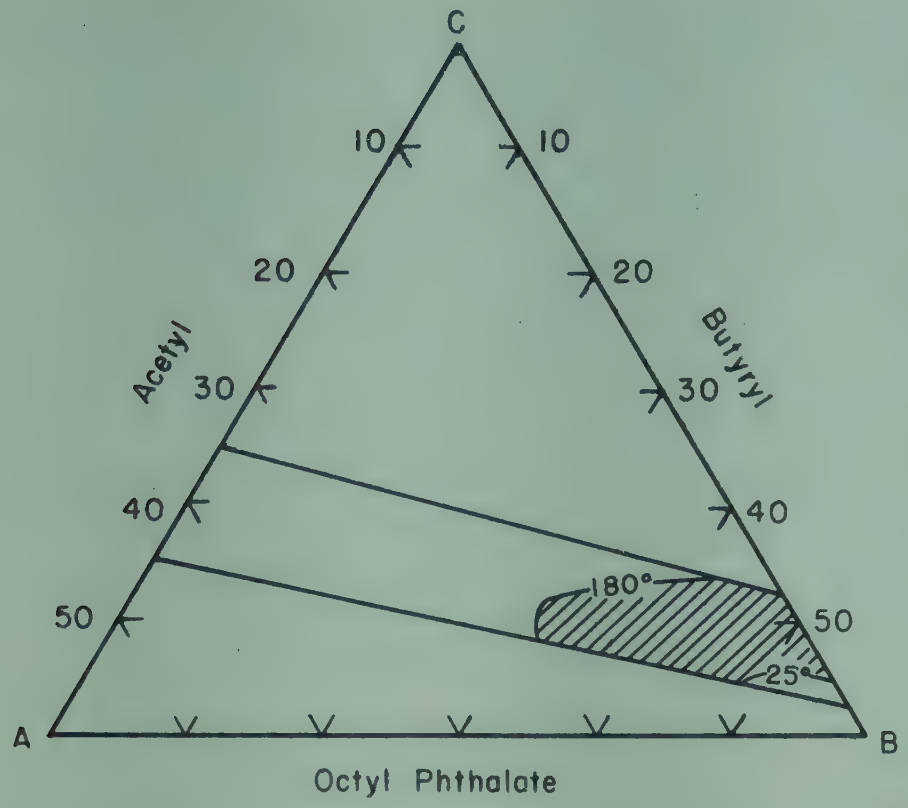

Fig. 29c. Relation of cellulose ester composition to solubility in octyl phthalate at 25° and 180 °C. (Malm, Fordyce, and Tanner[88]).

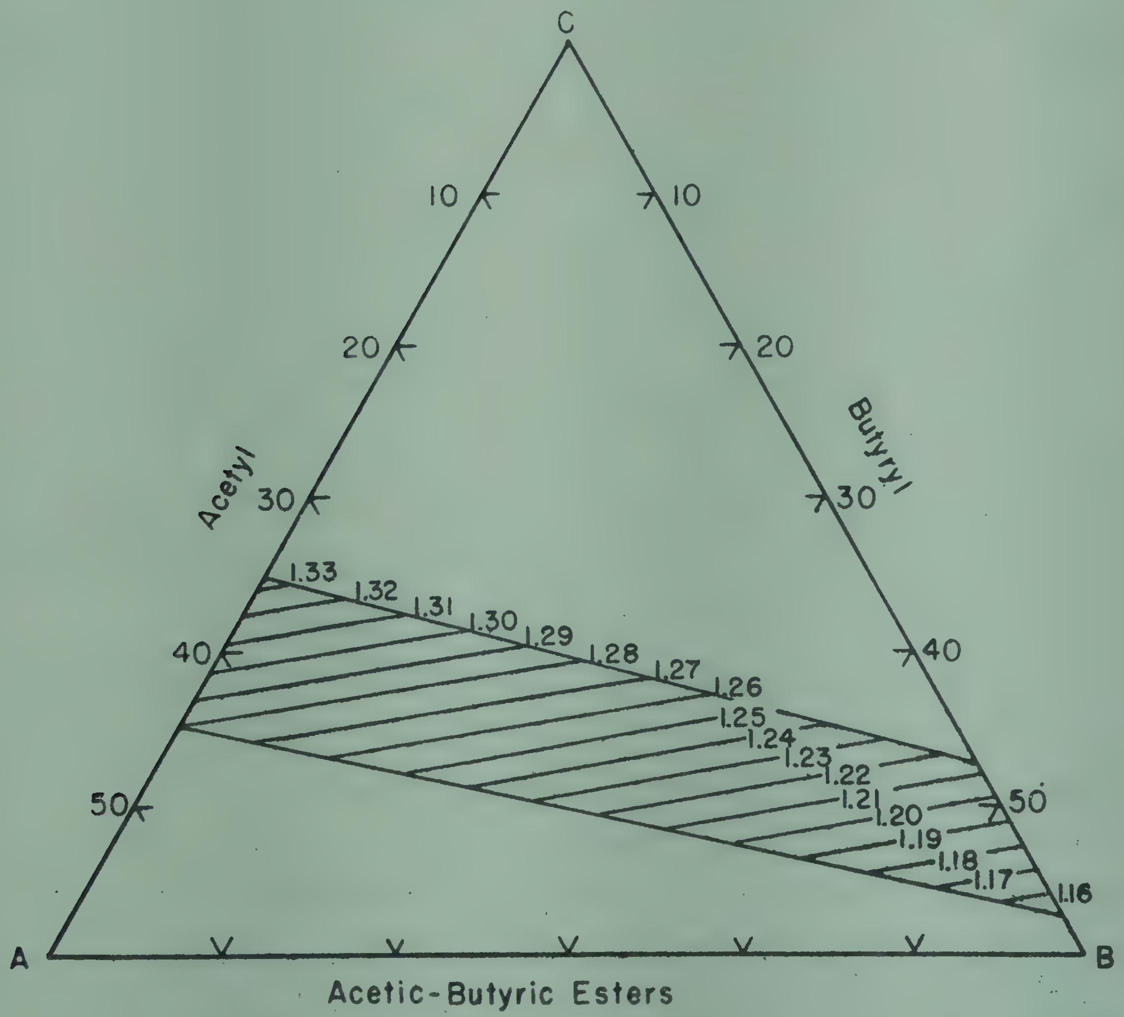

Fig. 30. Relation of cellulose ester composition and density (Malm. Fordyce. and Tanner[88]).

from the acetone-soluble range.) Sheeting compositions with higher amounts of plasticizer are being used for drawing and forming of plastic shapes. The triacetate has also been recommended as an electrical insulating material[89] because of its resistance to extended heating. Methylene chloride is still the commonest coating solvent, which means that solvent recovery and good ventilation are necessary economic and safety requirements.

Hydrolysis of cellulose triacetate produces esters which are acetone-soluble in the 36–42% acetyl range, have lower melting points, and have greater susceptibility to moisture and to textile dyes. Acetone has been the standard solvent for most uses, but several other readily available compounds, such as methyl acetate, ethyl lactate, diacetone alcohol, ethylene glycol monomethyl ether, and mixtures of ethylene dichloride with alcohols, are also used, as well as appreciable quantities of diluents, such as ethyl acetate, ethyl methyl ketone, and methyl, ethyl, and butyl alcohols.

Cellulose acetate yarn, manufactured by dry spinning from acetone solution, has been largely responsible for the great growth of acetate manufacture. Concentrated acetone solutions are forced through spinnerets to form filaments which are cured by circulated air, then gathered and passed over guide rolls to apply controlled twisting and stretching. The earliest descriptions of dry spinning of cellulose acetate were given in patents of Bayer and Co.,[90] although before that time wet-spinning processes, involving spinning of acetic acid or chloroform solutions into precipitating liquids, were described by Wagner[91] and by Little, Walker, and Mork.[91] The first large-scale manufacture of cellulose acetate rayon in the United States was in 1926. Rapid expansion continued from that time, resulting in an increase of from 2,620,000 pounds of acetate rayon manufactured in 1926 to nearly 10,000,000 pounds manufactured in 1930. The 1950 acetate yarn production was 443,000,000 pounds (326,000,000 pounds continuous filament and 117,000,000 pounds staple fiber).

New products have appeared on the market which are made by the incorporation of the coloring agent in the spinning solution. This coloring method allows a wider choice of light-stable dyes and yields products which are colored completely through the fiber.

Photographic film base made from acetone-soluble cellulose acetate, which replaced the hazardous cellulose nitrate for x-ray, portrait, and amateur Ciné, is now being replaced by the triacetate or by mixed esters. Acetone-soluble acetate is also used for the production of sheeting of high clarity and uniformity. This product is manufactured by flowing carefully filtered viscous solutions of the acetate in acetone onto a moving polished surface, and, after evaporation of solvent, continuously removing the film. Thicknesses down to 0.0002–0.0005 inch may be made. Films of greater thickness are made by solvent-laminating thinner gages, or by extrusion of pastes or plasticized pellets. Minimum amounts of solvent are used in paste extrusion of sheeting; the solvent must then be well removed to secure a dimensionally stable product. High-temperature extrusion is now widely used where the plasticizer serves as the solvent at temperatures of 250–450°F. Sheets, tubes, rods, and articles of various cross sections are made by this process. Plasticizers, such as methyl, ethyl, or methoxyethyl phthalates, which are solvents for the acetate at high temperatures, must be used. Sheet stock below 0.001 inch may be used as condenser dielectrics, thicker material (0.001–0.003 inch) for decorative wrapping and protective lamination, and still heavier gages (0.005–0.020 inch) for fabricating and hot-drawing of containers. Gages up to 0.125 inch are prepared by extrusion or skiving and may be used in forming processes, such as vacuum drawing.

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[89] W. Schröder, *Kunststoffe*, **32**, 82 (1942); *Bull. Inst. Paper Chem.*, **13**, 185 (1942–3).

[90] Bayer and Co., Brit. Patent 28,733 (Nov. 2, 1905); French Patent 350,422 (Jan. 4, 1906).

[91] A. Wagner, German Patents 137,255 (June 5, 1901); 152,432 (May 4, 1901); A. D. Little, W. H. Walker, and H. S. Mork, U. S. Patents 712,000 (Oct. 28, 1902); 792,149 (June 13, 1905).

Cellulose acetate compositions are commonly used in the thermoplastic molding field. Powdered ester is intimately mixed with plasticizer and pigment, and this mixture is fluxed on hot rolls. The cooled composition is granulated to furnish molding pellets which are generally handled by injection or extrusion molding. Since the acetates are high melting, fairly large amounts of plasticizer are required to produce compositions of reasonable flows. The higher acetyl esters of the acetone-soluble range give compositions of increased heat and moisture resistance. Molding of the triacetate has not been reduced to commercial practice.

Only minor quantities of cellulose acetate have been used in lacquers, mainly because of the limited solubility of the cellulose ester in suitable solvents and its incompatibility with most resins in quantities necessary to produce good adhesion and surface hardness.

Except in the textile field, mixed esters such as the acetate butyrates are more generally useful than the simple acetates. Against this fact must be balanced their higher cost. For photographic films, advantages are to be gained by the use of mixed esters containing sufficient quantities of higher acids to prevent undesirable curl with changes in humidity, at the same time keeping the higher acyl content within the range having satisfactory rigidity and tensile strength. The wider solubility of the mixed esters allows a balancing of solvents and nonsolvents in the coating composition so that film of excellent physical properties can be coated at high speeds.[92]

For manufacture of plastics, behavior toward plasticizers is a most important quality. Cellulose acetate requires comparatively high concentrations of active plasticizers for injection-molding operation, and those plasticizers which produce satisfactory flow characteristics are not retained as well as desired.[93] Here the mixed esters, particularly cellulose acetate butyrates containing a substantial amount of butyryl, offer distinct improvements; they possess greater compatibilities with plasticizers which show better retention characteristics, and they exhibit suitable flow with very

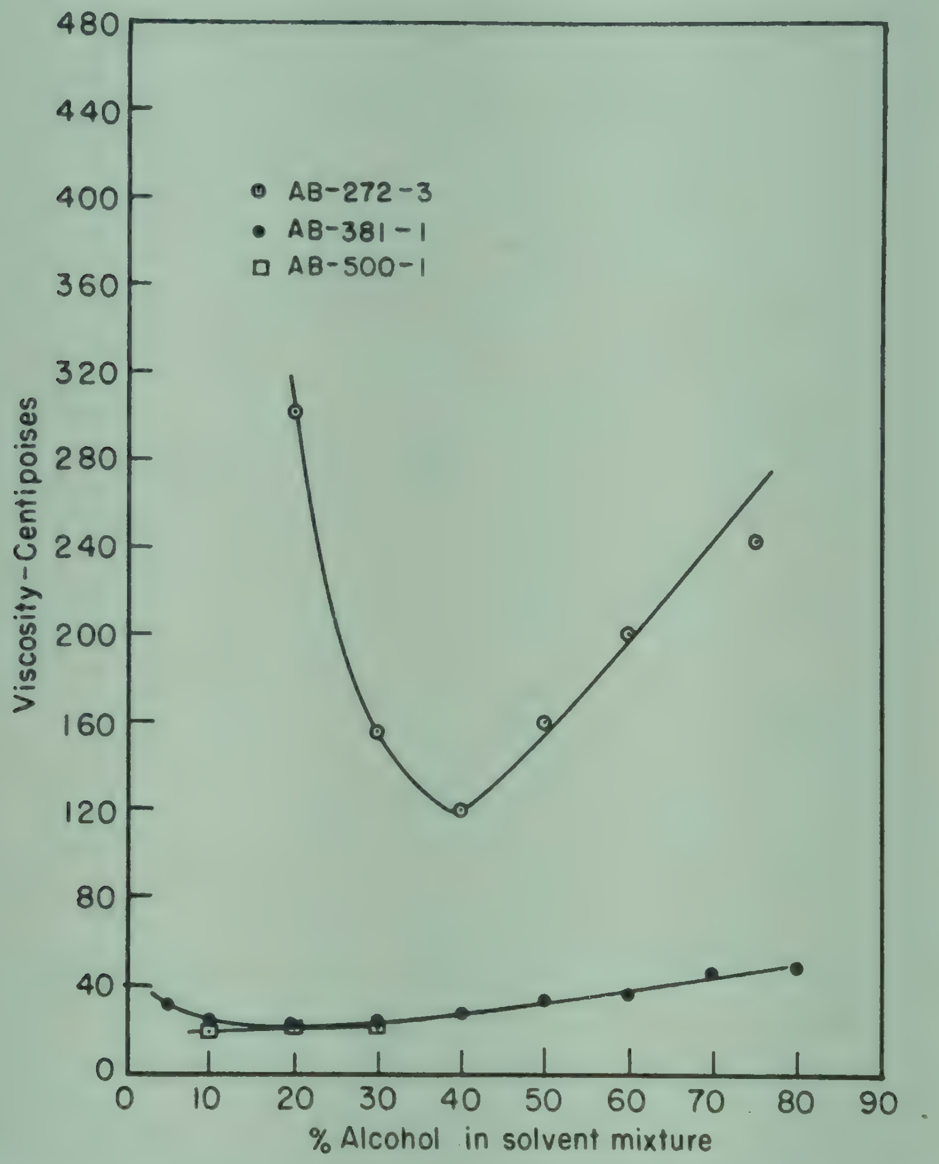

Fig. 31. Viscosity versus solvent composition, toluene–ethyl alcohol mixtures, 10% solids at 25°C. (Malm and Smith[97]). The first two numbers in the three-digit number following AB (acetate butyrate) refer to per cent butyryl. See text p. 808.

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[92] C. R. Fordyce and W. F. Hunter, Jr. (to Eastman Kodak Co.), U. S. Patents 2,319,051, 2,319,052, and 2,319,055 (May 11, 1943); *Chem. Abstracts*, **37**, 6129 (1943).

[93] C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, **32**, 1053 (1940).

small plasticizer concentrations. A cellulose acetate molding composition containing 49 parts of diethyl phthalate may thus be duplicated in flow characteristics by a cellulose acetate butyrate of 13% acetyl and 37% butyryl content with 15 parts of diamyl phthalate, the latter composition being much more permanent and dependable.

Compositions of high-butyryl cellulose acetate butyrate have been handled as molten compositions in coating paper and cloth.[94] This application requires esters of a high degree of heat stability compounded with modifying agents which are solvents at high temperature but which yield nontacky, compatible surfaces on cooling. Somewhat similar molten compositions have been used to give metal parts a melt dip coating for protec-

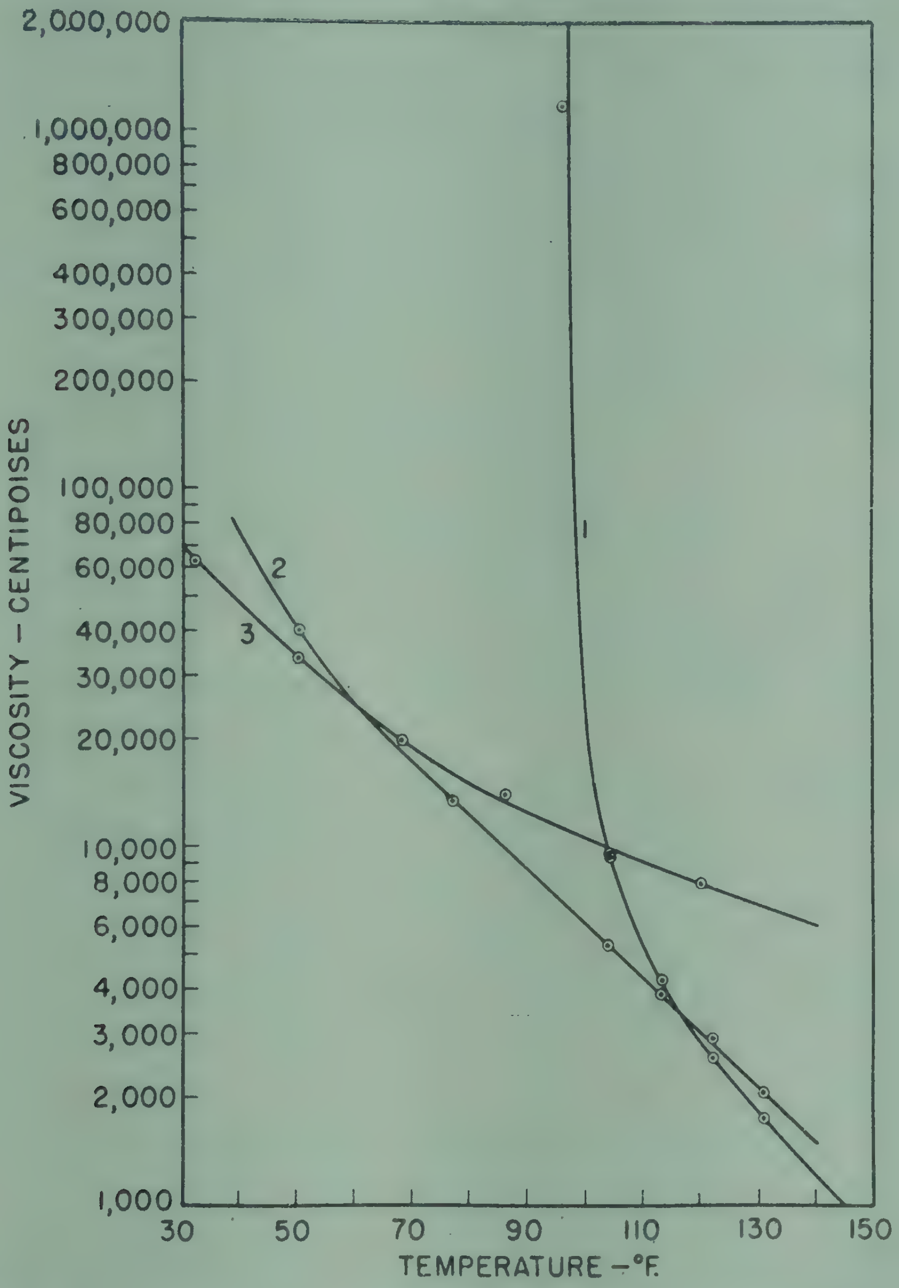

Fig. 32. Viscosity versus temperature for various lacquers (Malm and Smith[98]). 1, typical gel lacquer prepared from 38% butyryl ester; 2, nongelling lacquer prepared from 38% butyryl ester; 3, typical nitrocellulose solution in active solvents. See text p. 809.

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[94] C. J. Malm, M. Salo, and H. F. Vivian, *Ind. Eng. Chem.*, 39, 168 (1947).

tion against corrosion and abrasion.[95] Malm, Kaul, and Hiatt[96] studied the melt-viscosity curves of high-butyryl ester compositions and prepared quick-setting formulations which were used in melt-casting plastic articles without the use of pressure or volatile solvent.

The wider choice of volatile solvents for lacquers and film-forming solutions offered by mixed esters is, for many uses, an important factor. Esters, higher ketones, and mixtures of toluene with alcohols are among the common solvents used.

TABLE 11

Trends in Compatibility of Synthetic Resins with Cellulose Acetate Butyrate (Malm and Smith[97])

AB = acetate butyrate. The first two numbers in the three-digit numbers following AB refer to per cent butyryl.

Type of Resin	AB-161-2	AB-272-3	AB-381-1	AB-500-1
Alkyds Phenolics Ureas Maleics Polyesters	Compatibility depends on modifiers used in resins. Many resins of these types designed for lacquer use are compatible, particularly with type AB-381-1 ester.			
Aryl sulfonamide–formaldehyde condensates Modified hydrocarbons	← Compatibility very good →			
Chlorinated biphenyls	← Good →		← Very good →	
Acrylates	Fair	Good	Very good	Fair
Rosin derivatives	← Fair →		← Generally good →	
Polyvinyl acetates	Fair	Very good	Good	Poor
Polyvinyl chlorides Polyvinyl chloride-acetates Polyvinyl acetals	← Generally not compatible →			
Unmodified hydrocarbons Melamines Furfurals	← Generally not compatible →			
Alkyd resin plasticizers	Fair	← Generally good →		

As the butyryl content is increased, the solubility in inexpensive lacquer solvents increases as does the tolerance for common diluents.[97] Figure 31 shows the viscosity changes as ethyl alcohol is added to three acetate butyrates in toluene. The higher butyryl esters give low-viscosity solutions which tolerate considerable alcohol without appreciable viscosity increase. An acetate butyrate ester in the viscosity range of half-second nitrate has recently been put on the market for coating formulations.

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[95] C. J. Malm, H. B. Nelson, and G. D. Hiatt, *Ind. Eng. Chem.*, **41**, 1065 (1949).

[96] C. J. Malm, O. W. Kaul, and G. D. Hiatt, *Ind. Eng. Chem.*, **43**, 1094 (1951).

[97] C. J. Malm and H. L. Smith, Jr., *Ind. Eng. Chem.*, **41**, 2325 (1949).

The 38% butyryl ester has been worked into compositions which gel as the temperature is lowered ("gel lacquers"), which allow the application of heavy plastic coatings by a single dip into a warm lacquer.[98] Figure 32 shows the change in viscosity with temperature for (1) a gel-inducing solvent mixture, (2) a nongelling composition, and (3) a standard nitrocellulose formulation.

Reinhart and Kline[99] have found that a small amount of hydrolysis is desirable in cellulose mixed esters used for aircraft fabrics because of the more desirable effect of solvent mixtures on the physical properties of the products. Completely esterified esters became brittle upon exposure, while those with 0.2 to 0.4 free hydroxyl group for each glucose unit withstood exposure tests exceptionally well. Higher free hydroxyl group contents gave greater tautness fluctuation, causing coated fabrics to become slack in the rain.

Compatibility with resins is related to the amount of combined butyryl of the cellulose ester, the degree of hydrolysis, and the polarity and solubility of the resin class. Trends in compatibility are shown in Table 11[97] where the higher butyryl products show better properties except with the somewhat polar polyvinyl acetate.

Cellulose esters of higher aliphatic, substituted aliphatic, and aromatic acids, and mixed cellulose esters of these acids with lower aliphatic acids have received considerable attention, especially in patent literature. Products with very interesting properties have been described, but for economic reasons they have found no broad industrial application.

2. Other Aliphatic Esters

(a) UNSATURATED ESTERS

Preparation of cellulose esters of unsaturated aliphatic acids requires in general the same processes used for the corresponding saturated acids. Certain exceptions exist, however, in cases in which the unsaturated linkage interferes with normal behavior of the esterifying acid. Acrylic and methacrylic acids are difficult to employ as esterifying agents because of the ease with which these materials polymerize. Maxwell[100] has reported the preparation of mixed esters by reaction of methacrylic anhydride with cellulose acetate in the presence of sodium acetate at least equivalent in quantity to the methacrylic acid formed by the reaction.

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[98] C. J. Malm and H. L. Smith, Jr., *Ind. Eng. Chem.*, **38,** 937 (1946).

[99] F. Reinhart and G. M. Kline, *Ind. Eng. Chem.*, **32,** 185 (1940).

[100] R. W. Maxwell (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,175,357 (Oct. 10, 1939); *Chem. Abstracts*, **34,** 886 (1940).

Cellulose acetate methacrylate esters have been described[100a] in a preparation involving the treatment of an activated cellulose with methacrylic anhydride and sulfuric acid followed by an acetylation step. These mixed esters gel in solution when heated with benzoyl peroxide and form infusible copolymers when heated with acrylic monomers.

Crotonic acid tends to polymerize less readily and so can be used in a normal fashion to esterify cellulose. The triester may be prepared by treating purified cotton linters with acetic acid at room temperature, removing the activating acid with methylene chloride, and esterifying with crotonic anhydride in the presence of a sulfuric acid catalyst. The ester recovered by precipitation and washing in water is somewhat unstable to aging. Products held at room temperature for three months show loss in solubility. The addition of hydroquinone to the last wash prior to drying retards polymerization or cross-linking.

Mixed acetate crotonates are readily prepared either indirectly by treating a hydrolyzed cellulose acetate with crotonic anhydride and a catalyst or directly by treating cellulose with a mixed acid–anhydride bath. Crotonic acid is less reactive than butyric acid and in competition with acetic acid combines in smaller proportions than does butyric acid. Mixed acid–anhydride baths which in the acetate butyrate series would give 25, 38, and 50% butyryl contents give, respectively, 15–18, 29–35, and 42–47% crotonyl contents. Esters in the range of 40–50% crotonyl are quite resistant to acid hydrolysis. Acetate crotonates with 15–30% crotonyl are fairly readily hydrolyzed, but the change is largely at the expense of acetyl groups. In a typical case, as the weight per cent of acetyl changed from 29% to 19% (2 to 1.2 groups per glucose unit), the crotonyl changed from 18% to 21%, corresponding to 0.8 group per glucose unit in both cases.

The solubilities of the simple and mixed crotonate esters are similar to those of the corresponding butyrate esters. The compatibility with plasticizers is comparable, although the crotonate esters are less soluble in plasticizers than similar butyrate esters. Acetone solutions show little change in viscosity on standing even when benzoyl peroxide has been added. Films cast from these solutions are flexible but become brittle as the ester converts to an insoluble form. Heat or ultraviolet light[101] increases the conversion to the insoluble, cross-linked state. Esters high in crotonyl become insoluble after 24 hrs. at 100°C. Small quantities of benzoyl peroxide speed up the conversion. As the crotonyl content in mixed esters is lowered insolubilization by heat or light becomes slower.

[100a] A. A. Berlin and T. A. Makarova, *Zhur. Obshcheĭ Khim.* (*J. Gen. Chem.*), 21, 1267 (1951).

The vulcanizing of mixed esters containing methacrylyl and crotonyl groups has been described[102]; temperatures were in the range of 135–185°C., and sulfur and organic rubber accelerators were used. Textile fibers spun from these compositions and heated showed an improvement over acetate rayon in elastic recovery and resistance to dry-cleaning solvents.

Cellulose sorbates and acetate sorbates are prepared by the impeller method. Mixed esters containing combined sorboyl may also be made by including sorbic acid in ordinary esterification reactions. These dried esters lose solubility rapidly but are easily handled after treatment with hydroquinone before drying.

Cellulose undecylenate has been prepared by Gault and Urban[103] by treating hydrocellulose with the acid chloride and pyridine in the presence of toluene at 110–120°C. The impeller method (use of chloroacetic anhydride)[104] has also been used to prepare the simple ester; mixed acetate undecylenate esters may also be made from hydrolyzed cellulose acetate by this method. The double bonds of these esters are extremely reactive so that gelling of the reaction mixture is not unusual.

Higher unsaturated acids, such as oleic acid or mixed acids from vegetable oil saponification, may be used in the impeller or acid chloride reaction. Oleic acid esters are readily prepared, especially acetate oleate esters from acetone-soluble cellulose acetate as starting material. Although the finished esters are but slowly affected by heat or sunlight, the reaction mixture itself is subject to gelling. To secure esters with hydrolcarbon solubility, stearic acid may be used as an ingredient in the unsaturated acid mixture to reduce the gelling tendency during ester preparation. A mixture of stearic acid and 20–50% of linseed oil acids reacted with a hydrolyzed cellulose acetate yields an ester showing excellent solvent solubility and high sensitivity to heat or ultraviolet light. The use of carbon dioxide or nitrogen over the esterification reaction is an added precaution in preventing gelling.[105]

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[101] C. J. Malm and C. R. Fordyce (to Eastman Kodak Co.), U. S. Patent 1,973,493 (Sept. 11, 1934); *Chem. Abstracts,* **28,** 7013 (1934).

[102] M. L. Ernsberger and A. S. Gregory (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,396,165 (Mar. 5, 1946); *Chem. Abstracts,* **40,** 2984 (1946).

[103] H. Gault and M. Urban, *Compt. rend.,* **179,** 333 (1924).

[104] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patent 1,690,620 (Nov. 6, 1928); *Chem. Abstracts,* **23,** 512 (1929); U. S. Patent 1,739,210 (Dec. 10, 1929); *Chem. Abstracts,* **24,** 962 (1930).

Certain addition reactions are possible with the double bonds in these unsaturated cellulose esters. Chlorine and bromine will add to the crotonates dissolved in chloroform. About one-half of the theoretical amount adds in reactions in which excess of halogen is used.

Sulfur-containing derivatives have been made by heating a suspension of cellulose crotonate and sodium bisulfite in water or aqueous dioxane. The addition of sufficient groups leads to water-soluble derivatives.[106]

(b) HALOGEN-SUBSTITUTED ESTERS

The simple halogen-substituted cellulose esters are prepared with some difficulty. Cellulose treated with chloroacetic acid and anhydride in the presence of a zinc chloride catalyst slowly dissolves to give an almost completely substituted ester which is, however, degraded and of high color. Barnett,[107] using chloroacetyl chloride and a tertiary base, recovered similarly degraded derivatives. The di- and tri-chloroacetic acids are also reluctant to esterify cellulose. This characteristic behavior leads to the use of α-halogenated acid anhydrides as impelling agents in bringing about esterification of other carboxylic acids. Halogenated acids of more than five carbon atoms are more reactive with cellulose than the lower members, giving esters in the normal manner. Thus, α-halogen stearic acids, when reacted in the presence of chloroacetic anhydride,[108] readily esterify cellulose or its derivatives containing free hydroxyl groups.

The introduction of chlorine into cellulose acetate is much easier. Phosphorus pentachloride acts by substituting chlorine for some of the hydrogens of the acetyl groups.[109] Chloroacetyl may be added to acetone-soluble cellulose acetate by (a) direct reaction with chloroacetic anhydride and catalyst with or without an added solvent, (b) heating with chloroacetic acid, or (c) hydrolyzing in the presence of chloroacetic acid. The first reaction leads to products of minimum degradation and a high degree of substitution; the second is a degrading reaction and not efficient in introducing chloroacetyl; the third gives products low in both acetyl and chloroacetyl. Almost any desired cellulose acetate chloroacetate may be prepared by proper choice of the acetate starting material.[110] The resulting products are stable to heating at 180°C. for several hours. Their solubilities and compatibilities are comparable with those of acetate butyrates of similar composition. Since the chloroacetyl group is more resistant to hydrolysis than is the acetyl group, hydrolyzing the mixed ester in acid solution yields products relatively higher in chloroacetyl. A material analyzing 1.7 acetyl and 1.3 chloroacetyl groups per glucose unit was hydrolyzed to a product containing 0.4 acetyl and 0.7 chloroacetyl.[110] The acetate chloroacetates react readily in suspension or in solution with amines, such as pyridine, to form water-soluble quaternary salts. The reaction requires anhydrous conditions, and with large excesses of pyridine is essentially quantitative. This reaction on derivatives with a low amount of chloroacetyl has been claimed to improve acid-dyeing properties.[111]

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[105] C. J. Malm and G. D. Hiatt (to Eastman Kodak Co.), U. S. Patent 2,241,226 (May 6, 1941); *Chem. Abstracts*, **35**, 5315 (1941).

[106] H. Dreyfus (to Celanese Corp. of America), U. S. Patent 2,321,069 (June 8, 1943); *Chem. Abstracts*, **37**, 6893 (1943).

[107] W. L. Barnett, *J. Soc. Chem. Ind.*, **40**, 253T (1921).

[108] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patent 1,698,049 (Jan. 8, 1929); *Chem. Abstracts*, **23**, 1267 (1929).

[109] I. G. Farbenindustrie Akt.-Ges., Brit. Patent 306,132 (Feb. 17, 1928); *Chem. Abstracts*, **23**, 5040 (1929).

Izard and Morgan[112] described the preparation of an addition salt by treating acetate chloroacetates with sodium thiosulfate. Mild oxidation led to splitting out of sodium hydrogen sulfate with the formation of a disulfide linkage between two carbon atoms originally having the chlorine atom. Thiourea gave a similar addition reaction. Attempts to convert this intermediate to the disulfide failed because the acyl groups hydrolyzed under the required alkaline conditions.

Other halogen-containing esters may be prepared by adding chlorine or bromine to unsaturated esters dissolved in chloroform or tetrachloroethane.[113] When halogenated, cellulose crotonates, oleates, or esters containing unsaturated vegetable oil acids become more widely soluble and show an increase in moisture resistance.

(c) HYDROXY, KETO, AND AMINO ESTERS

The common low molecular weight carboxylic acids with a second functional group such as hydroxy, keto, or amino have not been successfully used to produce high degrees of esterification of cellulose. Hydroxy acids cannot be employed in ordinary esterification procedures without at the same time esterifying the hydroxyl group. Lactones, such as β-propiolactone, are reluctant to add to cellulose to form either an ether or an ester linkage. In general, α- and β-keto acids are unstable in the presence of anhydrides or catalysts used for esterification. Caldwell[114] described the preparation of cellulose acetate acetoacetates by treating a partially hydrolyzed acetate with diketene in the presence of pyridine. Higher keto acids, such as levulinic, may be used with the usual reaction methods employed for acids of comparable molecular weight. Although cellulose esters containing amino groups have been prepared indirectly by replacement of substituted halogen or tosyl (*p*-toluenesulfonyl), only Gardner[115] described a direct reaction. Hydrolyzed cellulose acetate is treated with N-acetylated amino acids in the presence of chloroacetic anhydride to yield derivatives whose nitrogen content makes them more susceptible to dyeing.

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[110] C. J. Malm, J. W. Mench, R. F. Williams, Jr., and G. D. Hiatt, *Ind. Eng. Chem.*, **42**, 1547 (1950).

[111] H. C. Olpin, S. A. Gibson, and J. E. Jones (to Celanese Corp. of America), U. S. Patent 2,348,305 (May 9, 1944); *Chem. Abstracts*, **39**, 617 (1945).

[112] E. F. Izard and P. W. Morgan, *Ind. Eng. Chem.*, **41**, 617 (1949).

[113] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patent 1,687,060 (Oct. 9, 1928); *Chem. Abstracts*, **22**, 4816 (1928).

Hydrolyzed cellulose esters containing minor quantities of combined hydroxy or keto acyl groups may be prepared by employing these acids as reaction media for hydrolysis of cellulose acetate.[116] This hydrolysis follows the behavior of equilibrium reactions, permitting a certain amount of interchange of acyl groups between the reaction solvent and the cellulose esters. The result is that some of the acyl groups from the hydrolysis solvent combine with cellulose, while a continual removal of acetyl groups from the cellulose ester takes place. The reaction may be carried out in the presence of a catalyst at a moderate temperature or with no added catalytic agent at higher temperatures. Cellulose acetate lactates, tartrates, pyruvates, and citrates may be made in this way. Several of the products are soluble in water. By the time much of the interchange acid has added, the total amount of combined acyl is quite low.

(d) ALKOXYACYL ESTERS

Acid chlorides of alkoxy fatty acids may be made to react with cellulose in the presence of pyridine to give soluble products, although there is usually difficulty in obtaining complete esterification. Cellulose derivatives with free hydroxyl groups may be quite readily esterified by reaction of either the acid chlorides or anhydrides of these acids in pyridine.[117]

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[114] J. R. Caldwell (to Eastman Kodak Co.), U. S. Patent 2,521,897 (Sept. 12, 1950); *Chem. Abstracts*, **45**, 860 (1951).

[115] T. S. Gardner (to Eastman Kodak Co.), U. S. Patent 2,461,152 (Feb. 8, 1949); *Chem. Abstracts*, **43**, 3616 (1949).

[116] C. J. Staud and C. S. Webber (to Eastman Kodak Co.), U. S. Patent 1,900,871 (Mar. 7, 1933); *Chem. Abstracts*, **27**, 3073 (1933).

[117] C. J. Malm and J. D. Coleman (to Eastman Kodak Co.), U. S. Patent 2,028,792 (Jan. 28, 1936); *Chem. Abstracts*, **30**, 1998 (1936).

In the presence of acid catalysts, anhydrides of alkoxyacetic acid are imilar to halogen-substituted acetic acids in that they do not react to ive cellulose derivatives. For this reason they may be employed similarly o chloroacetic anhydride as impelling agents to form esters of other organic cids.[6] As with hydroxyacetyl groups, small amounts of alkoxyacyl groups can be introduced by hydrolyzing a cellulose ester with an alkoxy fatty acid as solvent.[117a]

3. Miscellaneous Esters

(a) AROMATIC ACID ESTERS

There has been no commercial interest in cellulose esters of aromatic acids, investigation of their properties having shown no distinct advantages over the more readily prepared aliphatic esters. Cross and Bevan,[118] in the course of their researches on cellulose, prepared esters of benzoic acid by reaction of the acid chloride on alkali cellulose. Incomplete esterification was obtained, lower concentrations of reagents giving a fibrous monobenzoate whereas under more severe reaction conditions a solution of the dibenzoate resulted.

Cellulose tribenzoate was prepared by Wohl,[119] who used an excess of benzoyl chloride in pyridine at 110–130°C. with nitrobenzene as a diluent. Ost and Klein[120] investigated both caustic alkali and pyridine as reaction media for benzoylation. A pyridine reaction mixture was recommended as more satisfactory, giving products with 73% combined benzoic acid.

Atsuki and Shimoyama[121] prepared cellulose dibenzoate from both ordinary chemical cellulose and regenerated cellulose. After treatment with 35% alkali, the cellulose was aged 24 hrs. at ordinary temperature, then reacted with a benzene solution of benzoyl chloride at 50–60°C. for

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[117a] *Editors' Note:* The most noteworthy example of the mixed ester–ether category of cellulose derivatives is acetylated hydroxyethyl cellulose (I. G. Farbenindustrie Akt.-Ges., U. S. Patents 1,876,920 (Sept. 13, 1932) and 1,994,038 (Mar. 12, 1935); Carbide and Carbon Chemicals Corp., U. S. Patents 2,327,397 (Aug. 24, 1943) and 2,330,263 (Sept. 28, 1943)). At a hydroxyethoxyl substitution level of greater than 0.3, the triacetate derivatives have acetone solubility and exhibit lower water sensitivity than that of conventional acetone-soluble types of cellulose acetate. In general, hydroxyethyl cellulose is more reactive than cellulose itself in esterification reactions.

[118] C. F. Cross and E. J. Bevan, *Researches on Cellulose* **1895–1900**, Longmans, Green, London, p. 34.

[119] A. Wohl, *Z. angew. Chem.*, **25**, 285 (1903).

[120] H. Ost and F. Klein, *Z. angew. Chem.*, **26**, 437 (1913).

[121] K. Atsuki and K. Shimoyama, *Cellulose Ind.* (Tokyo), **2**, 336 (1926); *Kunstseide,* **0**, 250 (1928).

1–2 hrs. The product from regenerated cellulose was completely soluble in chloroform and acetone; that from normal cellulose gave poor solutions.

Benzoic acid in the presence of chloroacetic anhydride reacts to give cellulose tribenzoate. A recommended procedure is the reaction of 3 parts of cellulose, 15 parts of benzoic acid, 20 parts of chloroacetic anhydride, and 0.05 part of magnesium perchlorate for 8 hrs. at 60–70°C. The same reaction conditions may be employed for various substituted acids, including chloro-, nitro-, and methoxy-benzoic acids. The nitro- and halogen-substituted acids react with greater difficulty than benzoic; the *o*-methoxybenzoic derivative of cellulose is readily formed.[122] Cellulose cinnamate has been prepared both by reaction of the acid chloride in the presence of pyridine[123] and by esterification with the acid in the presence of chloroacetic anhydride.[3] Mixed esters have been prepared by the action of acetylvanillic acid and chloroacetic anhydride on a partially hydrolyzed cellulose acetate.[123a] Acetylvanillyl was introduced to the extent of 0.1 group per glucose unit.

Phenylacetyl chloride, when reacted upon cellulose in a mixture of pyridine and chlorobenzene at 80–120°C., yields an ester of 77% combined phenylacetic acid. The ester melts at 140°C.[85]

(b) DIBASIC ACID ESTERS

Cellulose may be esterified by one or both carboxyl groups of dibasic acids. Products of the latter type, such as are obtained by treatment of a pyridine solution of hydrolyzed cellulose acetate with a dibasic acid chloride or by using a mineral acid catalyst with a dibasic acid anhydride,[123b] are insoluble (cross-linked) and the products are of comparatively little commercial interest. If only one carboxyl group is combined with cellulose, the other may be converted to a salt, esterified by some other organic radical, or left in the free acid form. Products of all these types have been made.

Frank and Caro[124] prepared cellulose oxalic acid esters by reaction of acid chlorides of half-esters of oxalic acid with cellulose in the presence of yridine, with nitrobenzene as a diluent. The lower alkyl cellulose oxaates were found to be widely soluble in organic solvents. The cetyl ester was of more limited solubility and the menthyl ester was only partly soluble in all solvents.

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[122] H. T. Clarke and C. J. Malm (to Eastman Kodak Co.), U. S. Patent 1,704,283 (Mar. 5, 1929); *Chem. Abstracts*, **23**, 2033 (1929); Brit. Patent 313,408 (Aug. 27, 1929); *Chem. Abstracts*, **24**, 1217 (1930); Société Kodak-Pathé, French Patent 653,742 (Dec. 31, 1929); *Chem. Abstracts*, **23**, 3807 (1929).

[123] G. Frank and H. Mendrzyk, *Ber.*, **63B**, 875 (1930).

[123a] B. B. White and E. Barabash (to Celanese Corp. of America), U. S. Patent 2,581,565 (Jan. 8, 1952).

[123b] R. Rigamonti and V. Riccio, *Ann. chim.*, **42**, 283 (1952).

[124] G. Frank and W. Caro, *Ber.*, **63B**, 1532 (1930).

Similar products may be prepared by reaction of cellulose with the acid orm of the half-esters with chloroacetic anhydride as an impelling agent.[125] Cellulose alkyl succinates and phthalates have melting points below 200°C. nd are soluble in a wide variety of solvents[126] (Table 12).

Mixed esters prepared by esterification of the free hydroxyl groups of hydrolyzed cellulose acetate with dibasic half-esters also show wide solubilities (Table 13) and exhibit better film-forming properties than the simple esters.

Cellulose half-esters of dibasic acids with one carboxyl group in the acid form are best prepared by treating cellulose or cellulose acetates with a dibasic acid anhydride and a tertiary organic base. The reaction may be carried out on cellulose or partially hydrolyzed cellulose acetate.[127] Regenerated cellulose presoaked in water and then dewatered with pyridine s a satisfactory starting material for the simple ester. Acetate phthalates can be prepared by treating partially hydrolyzed cellulose acetates in a solvent such as acetone or dioxane with one and one-half times the theoretical quantity of phthalic anhydride and about two times the theoretical quantity of pyridine. These quantities are sufficient to add phthalyl to 60–70% of the available hydroxyl groups. Greater excesses of reagent will increase the amounts of phthalyl somewhat, but preparation of fully substituted derivatives is difficult even on repeated phthalation. The phthalate ester is recovered by diluting the viscous reaction solution and pouring it with stirring into acidified water which decomposes the pyridine salt.

Products of somewhat lower viscosity and combined dicarboxylic acid content may be made by heating cellulose acetate with a dicarboxylic acid anhydride in an inert solvent.[128] Melt reactions are also possible in which

[125] R. L. Stinchfield (to Eastman Kodak Co.), U. S. Patent 1,704,306 (Mar. 5, 1929); Chem. Abstracts, 23, 2033 (1929).

[126] C. J. Malm and C. R. Fordyce, *Ind. Eng. Chem.*, **32**, 405 (1940).

[127] C. J. Malm and C. R. Fordyce (to Eastman Kodak Co.), U. S. Patent 2,024,238 Dec. 17, 1935); *Chem. Abstracts*, **30**, 1230 (1936); F. Schulze (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,069,974 (Feb. 9, 1937); *Chem. Abstracts*, **31**, 2430 1937); C. J. Malm and C. E. Waring (to Eastman Kodak Co.), U. S. Patents 2,093,462 Sept. 21, 1937) and 2,093,464 (Sept. 21, 1937); *Chem. Abstracts*, **31**, 8194 (1937).

[128] L. B. Genung (to Eastman Kodak Co.), U. S. Patent 2,126,460 (Aug. 9, 1938); *Chem. Abstracts*, **32**, 7723 (1938); L. W. Blanchard, Jr., and C. L. Crane (to Eastman Kodak Co.), U. S. Patent 2,183,982 (Dec. 19, 1939); *Chem. Abstracts*, **34**, 2602 (1940).

TABLE 12. Properties of Cellulose Alkyl Esters of Dibasic Acids (Malm and Fordyce[126])

Ester of cellulose acetate with:	M.P., °C.	Solubility in							
		Acetone	Methyl ethyl ketone	Ethyl acetate	Butyl acetate	Ethylene chloride	Benzene	Toluene	Dioxane
Monomethyl succinate	195	+	+	+	−	+	−	−	+
Monoethyl succinate	128	+	+	+	−	+	+	−	+
Monopropyl succinate	108	+	+	+	+	+	+	+	+
Monobutyl succinate	106	+	+	+	+	+	+	+	+
Monomethyl phthalate	180	+	+	+	−	+	−	−	+
Monoethyl phthalate	178	+	+	+	+	+	+	−	+
Monopropyl phthalate	175	+	+	+	+	+	+	+	+
Monobutyl phthalate	155	+	+	+	+	+	+	+	+

TABLE 13. Properties of Cellulose Mixed Esters Containing Alkyl Dicarboxyl Groups (Malm and Fordyce[126])

Ester of cellulose acetate with:	M.P., °C.	Solubility in									
		Acetone	Methyl ethyl ketone	Ethyl acetate	Butyl acetate	Ethylene chloride	Benzene	Toluene	Benzene: alcohol, 2:1	Toluene: alcohol, 2:1	Dioxane
Monomethyl succinate	195	+	+	+	−	+	−	−	−	−	+
Monobenzyl succinate	175	+	+	+	−	+	−	−	−	−	+
Monomethyl phthalate	175	+	+	+	+	+	−	−	+	−	+
Monoethyl phthalate	...	+	+	+	+	+	−	−	+	−	+
Monobutyl phthalate	168	+	+	+	+	+	+	+	+	+	+

TABLE 14. Properties of Cellulose Acetate Phthalate of Varying Phthalyl Content (Malm and Fordyce[126])

Phthalyl content, %	M.P., °C.	Solubility in											
		Acetone	Methyl ethyl ketone	Ethyl acetate	Butyl acetate	Ethylene chloride	Benzene	Toluene	Benzene: alcohol, 2:1	Toluene: alcohol, 2:1	Dioxane	Dilute NH_4OH	Dilute NaOH
10	243	+	+	+	−	+	−	−	−	−	+	−	−
15	211	+	+	+	−	−	−	−	+	−	+	−	+
20	201	+	+	+	−	−	−	−	+	−	+	+	+
35	178	+	+	+	−	−	−	−	+	+	+	+	+

the hydrolyzed cellulose acetate is heated directly with an excess of the anhydride. Two parts of maleic anhydride melted with one part of an acetate of 32% acetyl content gives an acetate maleate containing 20% maleyl.[129]

The simple esters such as cellulose succinate or phthalate are readily soluble in organic solvents containing 5–20% of water and in various aqueous bases. Mixed esters prepared from cellulose acetate become increasingly soluble in organic solvents and in aqueous bases as the combined dibasic acid content is increased (Table 14). A product with about 1.4 acetyl, 0.8 phthalyl, and 0.8 hydroxyl degrees of substitution per glucose unit is soluble in a wide range of organic solvents and forms viscous aqueous solutions when dissolved by the gradual addition of the calculated quantity of sodium hydroxide or bicarbonate.[130] These solutions are most stable at a slightly alkaline pH. The viscosity may be increased by the careful addition of ions such as aluminum, zinc, magnesium, or calcium, or the ester may be completely precipitated by the addition of copper or mercury salt. The sodium salt may be precipitated by pouring the aqueous solution into excess acetone.

The acid esters are useful for application of water-insoluble surface coatings or sizings which are later to be removed by treatment with dilute aqueous alkali. The same property is used in the application of cellulose acetate phthalate as an antihalation backing in photography where the colored backing layer is removed as a water-soluble salt after treatment in the alkaline developer solution.[131] These esters are also being used in enteric coatings for medical purposes,[132,132a] since they are resistant to conditions encountered in the stomach but are soluble in the more alkaline medium of the intestinal tract.

Cellulose acetates containing small amounts of phthalyl or adipyl and treated with difunctional amines or with glycols are described as having better textile properties than the parent acetate.[133] Similar products containing small amounts of combined succinic, adipic, or sebacic acid introduced during the acetylation process are reported as giving improved elasticity.[134]

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[129] G. D. Hiatt and J. Emerson (to Eastman Kodak Co.), U. S. Patent 2,352,261 (June 27, 1944); *Chem. Abstracts*, **38**, 5671 (1944).

[130] C. J. Malm and C. R. Fordyce (to Eastman Kodak Co.), U. S. Patent 2,082,804 (June 8, 1937); *Chem. Abstracts*, **31**, 5578 (1937).

[131] C. J. Staud (to Eastman Kodak Co.), U. S. Patent 1,954,337 (Apr. 10, 1934); *Chem. Abstracts*, **28**, 3676 (1934).

[132] G. D. Hiatt (to Eastman Kodak Co.), U. S. Patent 2,196,768 (Apr. 9, 1940); *Chem. Abstracts*, **34**, 5602 (1940).

[132a] C. J. Malm, J. Emerson, and G. D. Hiatt, *J. Am. Pharm. Assoc., Sci. Ed.*, **40**, 520 (1951).

[133] H. Dreyfus (to Celanese Corp. of America), U. S. Patent 2,302,752 (Nov. 24, 1942); *Chem. Abstracts*, **37**, 2575 (1943).

(c) SULFONIC ACID ESTERS

Cellulose may be esterified by acid chlorides of organic sulfonic acids either in the presence of alkali or a tertiary organic base. Under acid conditions of reaction, the sulfonic acids do not esterify cellulose; they are on the other hand, suitable catalysts for certain esterification procedures.

Regenerated cellulose has been treated with a large excess of pyridine and benzenesulfonyl chloride to yield a soluble product.[134a] After 22 hrs. of reaction, the recovered ester contained two benzenesulfonyl groups per glucose unit. Only a small amount of combined chlorine was found.

Most published work on these derivatives has been concerned with esters of *p*-toluenesulfonic acid. Sakurada and Nakashima[135] studied the reaction of alkali cellulose with *p*-toluenesulfonyl chloride, obtaining best results at temperatures under 30°C. The degree of esterification for a single treatment corresponded to somewhat less than a monoester, although by repeated esterification products between mono- and di-esters were obtained.

Hess and Ljubitsch,[136] using pyridine as a reaction medium, obtained a product containing 12% chlorine and 1% nitrogen from reaction of cellulose and *p*-toluenesulfonyl chloride at 70°C. By use of cuprammonium rayon as a starting material and reaction at 15–20°C., an ester containing two tosyl (*p*-toluenesulfonyl) groups for each glucose unit and only 0.2% chlorine and 0.7% nitrogen was obtained. Hayes and Lin[137] heated a cellulose acetate *p*-toluenesulfonate in pyridine, 3-picoline, and isoquinoline and obtained about a 70% conversion of tosyl to the quaternary salt indicating that about 70% of the tosyl was combined with primary groups.

Bernoulli and Stauffer[138] attempted to avoid the side reactions by using the anhydride of *p*-toluenesulfonic acid in pyridine under a variety of conditions but obtained only a minor degree of esterification.

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[134] G. A. Richter, Jr. (to American Viscose Corp.), U. S. Patent 2,534,371 (Dec. 19, 1950); *Chem. Abstracts*, **45**, 2206 (1951).

[134a] I. V. Nemilova, *Zhur. Priklad. Khim.*, **25**, 1107 (1952).

[135] I. Sakurada and T. Nakashima, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **6**, 214 (1927).

[136] K. Hess and N. Ljubitsch, *Ann.*, **507**, 62 (1933).

[137] F. N. Hayes and C. H. Lin, *J. Am. Chem. Soc.*, **71**, 3843 (1949).

[138] A. L. Bernoulli and H. S. Stauffer, *Helv. Chim. Acta*, **23**, 627 (1940).

Rigby[139] has described a modified method for reaction of *p*-toluenesulfonyl chloride on alkali cellulose, employing first a temperature not above 20°C., then an elevated temperature up to 120°C. Esterification corresponding to 1.5 to 1.7 tosyl groups for each glucose unit was obtained. Large quantities of tosyl chloride and alkali were necessary.

Malm and Nadeau[140] prepared mixed esters by reaction of cellulose derivatives containing free hydroxyl groups with aromatic sulfonyl chlorides in the presence of pyridine. The products have better solubilities in organic solvents than the parent derivatives, and are highly resistant to moisture.

In recent years the *p*-toluenesulfonyl (tosyl) group has been used as a tool in studying the configuration of cellulose derivatives. Cramer and Purves[141] have shown that the tosyl group reacts most readily with the primary hydroxyl group of the cellulose, esterification beyond that point being at a considerably slower rate. The primary and secondary hydroxyl groups are distinguished by the relatively selective reaction of sodium iodide in acetone solution replacing the tosyl groups on primary hydroxyls by iodine. By preparation of tosyl derivatives of acetone-soluble cellulose acetate and treatment with sodium iodide, it was found that of the free hydroxyl groups in the cellulose acetate at least one-third were primary. Mahoney and Purves,[142] working with commercial ethyl celluloses, combined data from lead tetraacetate and periodate oxidation with tosylation followed by iodination values, and concluded that the first-order rate constants for tosylation of the unsubstituted hydroxyls were in a ratio of 2.3 for the second, 0.07 for the third, and 15 for the sixth position. In similar work on hydrolyzed cellulose acetate, Purves and Gardner[143] concluded that the available hydroxyls reacted in ratios of 2.16, 0.106, and 23.4 for the hydroxyls in the second, third, and sixth positions, respectively.

Malm, Tanghe, and Laird[144] studied the tosylation of hydrolyzed cellulose acetates. Extended reaction times gave increased amounts of tosyl but at a slower rate. Examination of a reaction curve allowed the choice of a point approximating the reaction of the primary hydroxyl. Hydrolyzed cellulose acetates showed a considerable variation in ratio of primary to secondary hydroxyl depending on the method of preparation.

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[139] G. W. Rigby (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,123,806 (July 12, 1938); *Chem. Abstracts*, **32**, 7263 (1938).

[140] C. J. Malm and G. F. Nadeau (to Eastman Kodak Co.), U. S. Patent 2,036,423 (Apr. 7, 1936); *Chem. Abstracts*, **30**, 3647 (1936).

[141] F. B. Cramer and C. B. Purves, *J. Am. Chem. Soc.*, **61**, 3458 (1939).

[142] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942).

[143] C. B. Purves and T. S. Gardner, *J. Am. Chem. Soc.*, **64**, 1539 (1942).

[144] C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Am. Chem. Soc.*, **70**, 2740 (1948).

Heuser and coworkers[145] reported on the tosylation of cellulose regenerated from the xanthate and concluded from iodination results that the rate constant for substitution on the primary hydroxyl was 5.8 times that for the secondary position.

Modification of the dyeing properties of cotton through introduction of tosyl groups followed by treatment with ammonia or amines was suggested by Karrer and Wehrli[146] since the tosyl radical is replaced by amino groups.

Hess and Ljubitsch[136] by treatment of ditosyl (di-*p*-toluenesulfonyl) cellulose with ammonia or ethylamine were not able to introduce over 2% nitrogen. Treatment of cellulose sulfonic esters with aliphatic primary or secondary amines to produce derivatives soluble in dilute acid has been patented by Haskins.[147]

The reaction solution with an amine as the solvent was allowed to stand at 20° to 65°C. for several days, yielding products which contained from 0.5 to 1 amino group for each glucose unit. The products obtained were insoluble in water but soluble in dilute acids which form amine salts. These reactions are similar to those with pyridine described above.[137]

Heating of an acetate *p*-toluenesulfonate, analyzing 0.196 primary and 0.054 secondary tosyls per glucose unit, in methanol with sodium methylate essentially removed the acetyl and *p*-toluenesulfonyl groups and produced 0.183 anhydro units per glucose unit in the cellulose. Reacetylation of the product supported this structure.[148]

Wolfrom, Sowden, and Metcalf[149] have prepared cellulose esters of methanesulfonic acid. Mercerized cotton or cellulose regenerated from the acetate treated in pyridine with methanesulfonyl (mesyl) chloride yielded products between the mono- and di-ester. They did not dissolve in the reaction mixture during preparation. Cellulose acetate of low acetyl content (1.7 acetyl groups) was reacted to introduce one mesyl group. This product, when treated with sodium iodide, gave a lower degree of iodine replacement than did *p*-toluenesulfonyl derivatives, contrary to that which might be expected from behavior of hexoses. The mesyl derivatives were also comparatively inactive toward replacement by ammonia.

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[145] E. Heuser, M. Heath, and M. H. Shockley, *J. Am. Chem. Soc.*, **72**, 670 (1950).

[146] P. Karrer and W. Wehrli, *Z. angew. Chem.*, **39**, 1509 (1926).

[147] J. F. Haskins (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,136,299 (Nov. 8, 1938); *Chem. Abstracts*, **33**, 1495 (1939).

[148] C. B. Purves and T. S. Gardner, *J. Am. Chem. Soc.*, **65**, 444 (1943).

[149] M. L. Wolfrom, J. C. Sowden, and E. A. Metcalf, *J. Am. Chem. Soc.*, **63**, 1688 (1941).

Mench[150] treated hydrolyzed cellulose acetates with N-alkyl and aryl sulfamyl chlorides and obtained products analyzing from 0.1 to 0.8 sulfamyl groups per glucose unit depending on the acetyl content of the starting acetate. In certain ranges of substitution water-soluble products were obtained.

(d) CARBAMIC ACID ESTERS

Carbamates of cellulose may be prepared by reaction of organic isocyanates upon dried cellulosic material in the presence of a tertiary base such as pyridine. Completely anhydrous reaction conditions are necessary; otherwise the water, in a rather violent reaction, will consume two molecular equivalents of isocyanate to form substituted ureas which are generally quite difficult to remove from the substituted cellulose.

The reaction of cellulose and partially hydrolyzed cellulose acetates with alkyl and aryl isocyanates has been studied by Hearon, Hiatt, and Fordyce.[151] The reaction of carbamic acid itself gave products of low nitrogen content. Methyl and ethyl isocyanates gave partial reaction with hydrolyzed cellulose acetates but failed to give fully esterified products in reactions at 50° and 100°C. Aromatic isocyanates reacted readily to give fully esterified products and, with the use of less than the theoretical quantities of phenyl isocyanate, reacted quantitatively. The reaction of cellulose with excess isocyanate was slower but gave, after 48 hrs. at 100°C., soluble products which were relatively undegraded and proved on analysis to be the tricarbamates.

A second paper[152] reported that hydrolysis experiments were carried out to remove acetyl groups from cellulose acetate carbamates to produce simple cellulose carbamates with some hydroxyl groups. This was possible because of the much greater alkali stability of the carbamate group. Series of cellulose carbanilates and α-naphthyl carbamates were prepared and their solubilities described.

Schneebeli[152a] studied the reaction of phenyl isocyanate with cellulose in pyridine as a function of time and temperature. X-ray studies showed that reaction did not occur within the crystalline portion until one-quarter to one-third of the hydroxyl groups had reacted. Dyer and McCormick[153] added *o*- and *p*-chlorophenyl isocyanates to methyl cellulose and got complete substitution in 6 hrs. at 65°C. They reported only a small amount of degradation.

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[150] J. W. Mench (to Eastman Kodak Co.), U. S. Patent 2,518,706 (Aug. 15, 1950); *Chem. Abstracts*, **45**, 1768 (1951).

[151] W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *J. Am. Chem. Soc.*, **65**, 829 (1943).

[152] W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *J. Am. Chem. Soc.*, **65**, 833 (1943).

[152a] P. Schneebeli, *Compt. rend.*, **234**, 738 (1952).

The reaction of hydrolyzed cellulose acetate with different aryl isocyanates was examined by Hearon and Lobsitz.[154] Rated in order of increasing reactivity, these materials were *o*-tolyl, *p*-tolyl, phenyl, α-naphthyl, *o*-chlorophenyl, and *p*-bromophenyl isocyanate.

Some attempts have been made to improve cellulose acetate products by treatment with diisocyanates. Hydrolyzed acetates treated with hexamethylene diisocyanate are claimed to show an improvement for textile uses because of their decreased organic solvent solubility and increased ironing temperature.[155]

High molecular weight isocyanates such as those from hydrogenated rosin have been added to cellulose derivatives to effect an improvement in solubility, compatibility, and resistance to hydrolysis.[156]

Breslow[157] has produced acid-soluble derivatives by treating ethyl cellulose, cellulose acetate, and hydroxyethyl celluloses with isocyanates or azides of tertiary bases. Nicotinyl azide reacted under nitrogen in the presence of pyridine to give products soluble in dilute acetic acid. Similar solubility resulted from treating hydroxyethyl cellulose with *p*-(dimethylamino)phenyl isocyanate.

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[153] E. Dyer and K. L. McCormick, *J. Am. Chem. Soc.*, **68**, 986 (1946).

[154] W. M. Hearon and J. L. Lobsitz, *J. Am. Chem. Soc.*, **70**, 296 (1948).

[155] D. D. Coffman and J. S. Reese (to E. I. du Pont de Nemours & Co.), Brit. Patent 548,807 (Oct. 26, 1942); *Chem. Abstracts*, **38**, 485 (1944).

[156] D. S. Breslow (to Hercules Powder Co.), U. S. Patent 2,492,928 (Dec. 27, 1949); *Chem. Abstracts*, **44**, 2238 (1950).

[157] D. S. Breslow, *J. Am. Chem. Soc.*, **72**, 4244 (1950).

D. ALKALI AND OTHER METAL DERIVATIVES

W. D. Nicoll, N. L. Cox, and R. F. Conaway

The treatment of cellulose fibers with alkalies is one of the oldest and most important commercial reactions of cellulose. Although this broad field has been the subject of investigation for more than 100 years, the effects of alkali on cellulose fibers are not yet fully understood. There are two important objectives in treating cellulose with alkalies, namely, to modify the physical and chemical properties of natural fibers such as in mercerization, and to obtain intermediates such as alkali cellulose for conversion to cellulose derivatives.

The simplest classification of the alkali metal–cellulose complexes is the following: alkali cellulose, the true metal alcoholates of cellulose, cuprammonium- and cupriethylenediamine–cellulose complexes, and cellulose–organic base complexes. The organic nitrogen bases by definition are out of place in this chapter but are included since their action on cellulose is similar to that of the inorganic bases.

1. Alkali Cellulose

Strong alkali solutions acting on cellulose at low or room temperatures produce alkali cellulose. This treatment of cellulose has been known by the textile industry for a very long time as "mercerization,"[1] so called after John Mercer who discovered the process in 1844.[2]

The technical use of alkali cellulose dates from the discovery of Lowe[3] in 1889 that tension on cellulosic fibers during treatment with strong alkali increased luster, and from the even more important discovery of Cross, Bevan, and Beadle[4] in 1892 that treatment of alkali cellulose with carbon disulfide produced cellulose xanthate which could be dissolved in water or dilute alkali to form an orange-yellow viscous solution which they termed "viscose." As a result of this discovery, the preparation of alkali cellulose (or "soda cellulose" as it is sometimes named) became the first step in the manufacturing operations of the important group of viscose industries from which modern civilization derives such varied products as rayon, cellophane, cellulose sponges, cellulose sausage casings, and certain types of bottle closures.

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[1] D. A. Clibbens, *J. Textile Inst.*, **14**, T217 (1923).

[2] E. A. Parnell, *Life and Labors of John Mercer*, Longmans, Green & Co., London, 1886.

[3] H. A. Lowe, Brit. Patents 20,314 (1889); 4452 (Dec. 22, 1890).

[4] C. F. Cross, E. J. Bevan, and C. Beadle, *J. Chem. Soc.*, **63**, 837 (1893).

In addition to its use in the preparation of viscose, alkali cellulose is an important intermediate product in the preparation of certain cellulose ethers, such as the ethyl, methyl, and benzyl ethers, which find application in the preparation of films and many types of plastic products. Mercerization is also used as a finishing treatment for textiles, and in the preparation of certain types of highly absorptive papers and paperboard products now employed in the manufacture of such materials as shoe lasts and blotting papers. This discussion on the nature of alkali cellulose and its applications in industry will be presented mainly from the standpoints of the viscose process and the mercerization of textile fibers.

(a) STRUCTURE OF ALKALI CELLULOSE

Mercer assumed that the formation of alkali cellulose is a result of chemical combination between the cellulose and sodium hydroxide, and that the resulting compound is susceptible to decomposition under the action of water. Karrer[5] in support of this view cited analogous cases of simple and polyhydric alcohols and pointed out that many of these alcohols form compounds of a characteristically complex nature with alkali. Other workers, however, have held that the changes involved when cellulose is treated with alkali are purely physical and similar to those produced in the swelling of many other colloidal substances. Emphasis in recent years has been given to the methods of x-ray analysis as a means of determining the changes occurring when alkali cellulose is formed, and this method of investigation appears to give definite support to the view that cellulose may form not only one, but several, compounds with strong alkalies. The particular compound formed depends on the type of cellulose, the concentration of alkali in solution, and the temperature. But regardless of the type of compound formed, alkali celluloses decompose readily on washing with water, and the caustic can be easily and completely removed.

Assuming a chemical compound as the more probable form for alkali cellulose, two views are possible. Either the cellulose, like the simple alcohols and certain other polyhydric compounds, forms a true alcoholate with a metal ion (M) substituting for a hydrogen ion, thus:

$$R_{cell}(OH) + MOH \longrightarrow R_{cell}(OM) + H_2O$$

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[5] P. Karrer, *Cellulosechemie*, 2, 125 (1921).

or the alkali is present as an addition complex such as is believed to form between certain sugars and the alkaline earth hydroxides. In the latter case, alkali cellulose would have the composition represented by $R_{cell}(OH)_x \cdot (MOH)_y$. Although the literature indicates differences in opinion on this point, the majority of investigators in this field seem to agree that, at least in the presence of water, the addition complex is to be preferred over the alcoholate type of structure. It is interesting to note that using one of the latest methods for studying this question, Makolkin[6] was able to follow the isotope exchange of oxygen 18 between water and alkali cellulose and decided that mercerization proceeds according to the equation:

$$R_{cell}(OH) + NaOH \longrightarrow R_{cell}(OH) \cdot NaOH$$

Thus, alkali cellulose is a product of the addition of alkali to cellulose in the form of a weak electrolyte and not in the form of an alcoholate.

Another controversial point concerns the question of whether more than one addition complex may exist, with many investigators agreeing on $(C_6H_{10}O_5)_2 \cdot NaOH$ as correctly representing the composition of the alkali cellulose commonly formed in alkali solutions of 12 to 18% concentration. A second compound has been given the formula $C_6H_{10}O_5 \cdot NaOH$ and variously reported as existing in solutions containing 20 to 40% NaOH. X-ray evidence strongly supports the existence of a new crystalline structure in caustic soda solutions of about 21% concentration, but the results from other methods used in examining these compounds have not been consistent.

In this connection it should be kept in mind that different celluloses contain different ratios of crystalline to noncrystalline material. This affects the number of cellulose chains available for reaction, and, therefore, influences not only x-ray results but also those obtained by other methods.

Important reasons for the divergent views which have been expressed in regard to the structure of alkali cellulose include differences in the types of celluloses investigated, the colloidal nature of alkali cellulose, and the widely different concepts held in regard to the basic nature of the swelling process. Following the discovery of the preferential absorption of alkali by cellulose in contact with solutions containing more than 12% of NaOH, early investigators concentrated attention on this fact and tended to disregard swelling phenomena and the role played by water in the formation of alkali cellulose. More recently, it was recognized that considerable quantities of water accompany the alkali into the solid cellulose phase, and emphasis shifted to the ratio of water to the total amount of alkali present, as well as to the degree of swelling and accompanying increase in internal surface. For example, studies by Saito[7] have helped to clarify complex relationships existing between the total amounts of alkali and water absorbed and how these relationships are influenced by such variables as the type of cellulose, the kind and concentration of alkali, the temperature, and even the addition of an inert substance such as sodium chloride. This and similar work will be discussed in more detail later. In general, support is given to the view that physical factors probably have a greater influence on the properties of alkali cellulose than does any stoichiometric relationship which may exist between cellulose and combined alkali. However, because of the immense amount of work done to acquire exact knowledge of the quantitative relationship in the system cellulose–sodium hydroxide–water, a brief review of some of the methods which have been used to study this problem seems justified.

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[6] I. A. Makolkin, *J. Gen. Chem.* (*U. S. S. R.*), **12,** 365 (1943); *Chem. Abstracts*, **37,** 3418 (1943).

(b) METHODS FOR DETERMINING ALKALI ABSORBED

(*1*) *The Direct Method*

The first investigator to attempt to determine the amount of caustic soda taken up by cellulose was Gladstone,[8] who in 1852 treated cotton with various concentrations of sodium hydroxide and then washed the samples with cold absolute alcohol or hot alcohol of about 92.5% concentration until constant weight was obtained. Similar experiments were made with potassium hydroxide, and Gladstone concluded that each of these alkalies forms definite compounds with the cellulose. The method of washing with alcohol has since been reinvestigated by several other experimenters who have used either the same or slightly improved modifications of Gladstone's original method. Rassow and Schwarze,[9] for example, found that results obtained by washing with alcohol depend to a great extent on the alkali content of the solution, the water content of the alcohol, and the selection of the proper indicator to determine the completion of the washing operation. The conclusion was reached that a compound containing 12.3 g. of NaOH per 100 g. of cellulose and corresponding to the formula $(C_6H_{10}O_5)_2 \cdot NaOH$ is formed in alkali solutions containing from 18 to 40%

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[7] G. Saito, *J. Soc. Chem. Ind., Japan*, **43**, B126, B133, B160, B194 (1940); **44**, B89 (1941); *Cellulosechemie*, **18**, 106 (1940).

[8] J. H. Gladstone, *J. Chem. Soc.*, **5**, 17 (1852).

[9] B. Rassow and K. Schwarze, *Papier-Fabr.*, **28**, Tech.-wiss. Tl., 693, 746 (1930).

NaOH. Still more recently Rogovin[10] substituted butyl or propyl alcohol or ethyl alcohol because these solvents reduce hydrolysis of "soda cellulose." He concluded that the amount of alkali combined is greater than that indicated above.

Bancroft and Calkin[11] have criticized Gladstone's method, stating that it is not proof of compound formation since the use of alcohol only introduces another variable, and the results merely indicate how much sodium hydroxide is retained by the sample under the conditions of washing used. If this conclusion is correct, it is surprising that the results obtained by Gladstone and certain other workers agree so well with those from at least two other methods, namely, the change-in-titer and change-in-x-ray-diffraction-pattern, both of which have been interpreted to indicate the formation of a cellulose–alkali compound.

(2) *The Indirect or Change-in-Titer Method*

The most widely studied method of determining the composition of alkali cellulose is that introduced by Vieweg[12] in 1907. It consists in determining by titration the change in alkali concentration when a known weight of cellulose is placed in either a known volume or known weight of alkali solution. The method requires careful standardization of the experimental conditions in order to obtain reproducible results. Heuser and Niethammer[13] recommended a ratio of at least 10:1 for alkali solution to cellulose, and Rassow and Schwarze[9] showed that absolutely dry cellulose should not be used in measuring absorption because the process will then be nonuniform.

Probably the most persistent criticism which has been made of the indirect method is that made first by Leighton,[14] namely, that no attention is given to the very considerable swelling and hydration which occur when cellulose is treated with strong solutions of alkali. This criticism, however, has generally been made by those interested in the total quantity of alkali absorbed by the cellulose and is not believed justified when only the preferentially absorbed alkali is to be determined. This point is further discussed below in connection with the work of Sharkov and Saito.

[10] Z. A. Rogovin, *Trudy Konferentsiĭ Vysokomolekulyar. Soedineniyam, Akad. Nauk S. S. S. R., Otdel. Khim. Nauk i Otdel. Fiz.-Mat. Nauk,* **1,** 33 (1943) (Pub. 1945); through *Chem. Abstracts,* **40,** 457 (1946).

[11] W. D. Bancroft and J. B. Calkin, *Textile Research,* **4,** 119, 159 (1934); *J. Phys. Chem.,* **39,** 1 (1935).

[12] W. Vieweg, *Ber.,* **40,** 3876 (1907); **41,** 3269 (1908); **57B,** 1917 (1924).

[13] E. Heuser and W. Niethammer, *Cellulosechemie,* **6,** 13 (1925).

[14] A. Leighton, *J. Phys. Chem.,* **20,** 32, 188 (1916).

The results obtained by use of the Vieweg indirect method may most readily be discussed by referring to the curve formed by plotting the apparent change in alkali absorption against the caustic soda content of the treating solution. This curve, generally known as the Vieweg curve,[15] has the following characteristics (Fig. 33): It shows a gradual increase in alkali absorption with increased concentration of caustic soda from 0 to 13–16% NaOH; at this point there occurs a definite break in the curve followed by a region of constant absorption up to a concentration of approximately 21% NaOH; above this the curve again rises gradually but flattens off at a new level in the range of 35–40% NaOH. Richardson and Maass[16] made a study of the absorption of alkali from concentrated solutions, and, on the basis of their work and that of Rumbold[17] and Vieweg, constructed a curve which shows the absorption of alkali over the whole range of 0 to 50% concentration (Fig. 34).

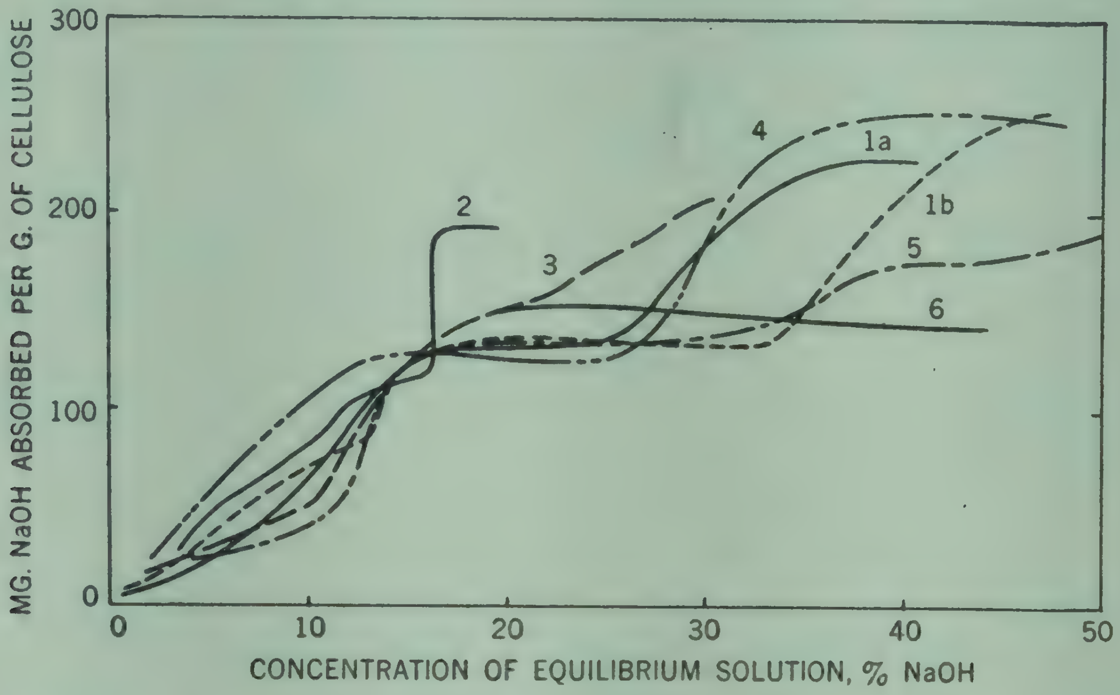

Fig. 33. Alkali preferentially absorbed by cellulose as determined by various investigators using the change-in-titer method (d'Ans and Jäger[15]). Curves: 1a, Vieweg I; 1b, Vieweg II; 2, Liepatoff; 3, Rassow and Wadewitz; 4, Dehnert and König; 5, Heuser, Niethammer, and Bartunek; 6, Karrer and Nishida.

The amount of alkali absorbed at the first break in the Vieweg curve has been determined by different investigators and may be said to average about 13 g. of NaOH per 100 g. of cellulose. The absorption at the second break is approximately 22.5 g. of NaOH per 100 g. of cellulose. Vieweg, and many other investigators who have used the method more recently, concluded that the first break in the curve denoted the formation of a definite compound, $(C_6H_{10}O_5)_2 \cdot NaOH$, which is stable throughout the range of alkali concentration represented by the first flat portion of the curve. Evidence for the formation of the second compound, $C_6H_{10}O_5 \cdot NaOH$, in concentrations of caustic soda above 35% is not so clear, and several investigators following Vieweg were unable to obtain any absorption values sufficiently high to substantiate the existence of this compound.

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[15] J. d'Ans and A. Jäger, *Cellulosechemie*, **6**, 137 (1925).

[16] R. Richardson and O. Maass, *J. Phys. Chem.*, **36**, 3064 (1932).

[17] J. S. Rumbold, *J. Am. Chem. Soc.*, **52**, 1013 (1930).

The theory of compound formation and the use of the Vieweg method for determining alkali absorbed by cellulose has been vigorously attacked from a theoretical standpoint on the grounds that the curve does not conform to phase-rule requirements. Leighton[14] was the first to point this out, and it has since been discussed by Bancroft and Calkin.[11] According to these investigators, the alkali absorption curve should show a distinct vertical portion rather than a horizontal portion, as evidence for compound formation. As ordinarily determined, the curve does not show this, but rather shows a gradual rise to the inflection point. An important factor not recognized by the critics of the Vieweg curve is that the system under investigation is one containing a high-molecular-weight material having characteristically colloidal properties. In such a system swelling is not uniform, and one should expect that as swelling progresses there would be a gradual increase in the amount of reactive surface available for compound formation and that this would preclude the possibility of obtaining a sharp vertical rise in the absorption curve. These ideas are in accord with a view

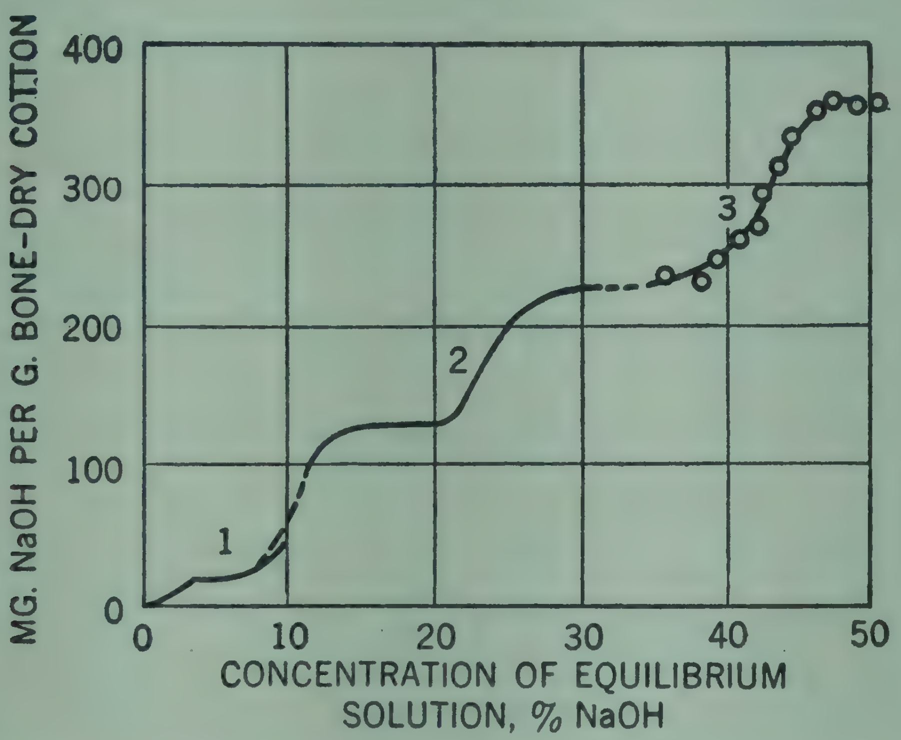

Fig. 34. Composite curve for alkali preferentially absorbed by cotton at 20°C. (Richardson and Maass[16]). Curves: 1, Rumbold; 2, Vieweg; 3, Richardson and Maass.

recently expressed by G. and T. Petitpas.[18] Even if all of the cellulose chains are equally available, the extent of reaction will be a continuous function of the alkali concentration, and the alkali absorption curve will have the same shape as the titration curve of a polybasic acid if more than one type of addition complex of NaOH with cellulose is found. Calkin,[19] independently, applied the x-ray method to the system and found that the change in x-ray diffraction diagram from native cellulose to that characteristic of alkali cellulose takes place only gradually, starting in a caustic soda solution of about 13% concentration and becoming complete at about 16% NaOH. This range, it will be recognized, coincides closely with that immediately preceding the break in the Vieweg curve. It seems likely, therefore, that the change in x-ray diffraction pattern and the gradual rise in the absorption curve for alkali may be due to one and the same phenomenon.

(3) *The Blotting or Centrifuging Method*

Another method which has been used for investigating the cellulose–caustic soda–water system is to blot or to centrifuge off the excess alkali solution and to determine the total alkali and water taken up by the cellulose. A general criticism of these methods is that it is difficult to determine accurately the point at which excess alkali solution clinging to the surfaces of the fibers is removed. It is also difficult to avoid loss of water vapor which conceivably would affect the final results. Both the blotting and centrifuging methods fail to take into account water absorbed by the cellulose itself as differentiated from water accompanying the alkali as solvent. Nevertheless, useful information regarding both the absorption and swelling processes has been gained from this sort of work.

Beadle and Stevens,[20] among the first to use the blotting method, studied particularly the effects of temperature and the concentration of the caustic soda solution. These experimenters used regenerated cellulose in the form of cuprammonium rayon, and their results (Fig. 35) show that, for temperatures between 5° and 40°C., points of maximum hydration and maximum alkali absorption occur, and that these maxima are greater at lower temperatures. For solutions of 3 to 9% alkali content, the effects of temperature on hydration and on caustic soda absorbed bear a close resemblance to each other (the shapes of the curves are relatively much alike), indicating that under these conditions the solutions in which the cellulose was immersed were absorbed without change in composition. For the more concentrated solutions (10–25% NaOH) the curves

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[18] G. and T. Petitpas, *Compt. rend.*, **226**, 672 (1948).

[19] J. B. Calkin, *J. Phys. Chem.*, **40**, 27 (1936).

[20] C. Beadle and H. P. Stevens, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **13**, 25 (1912).

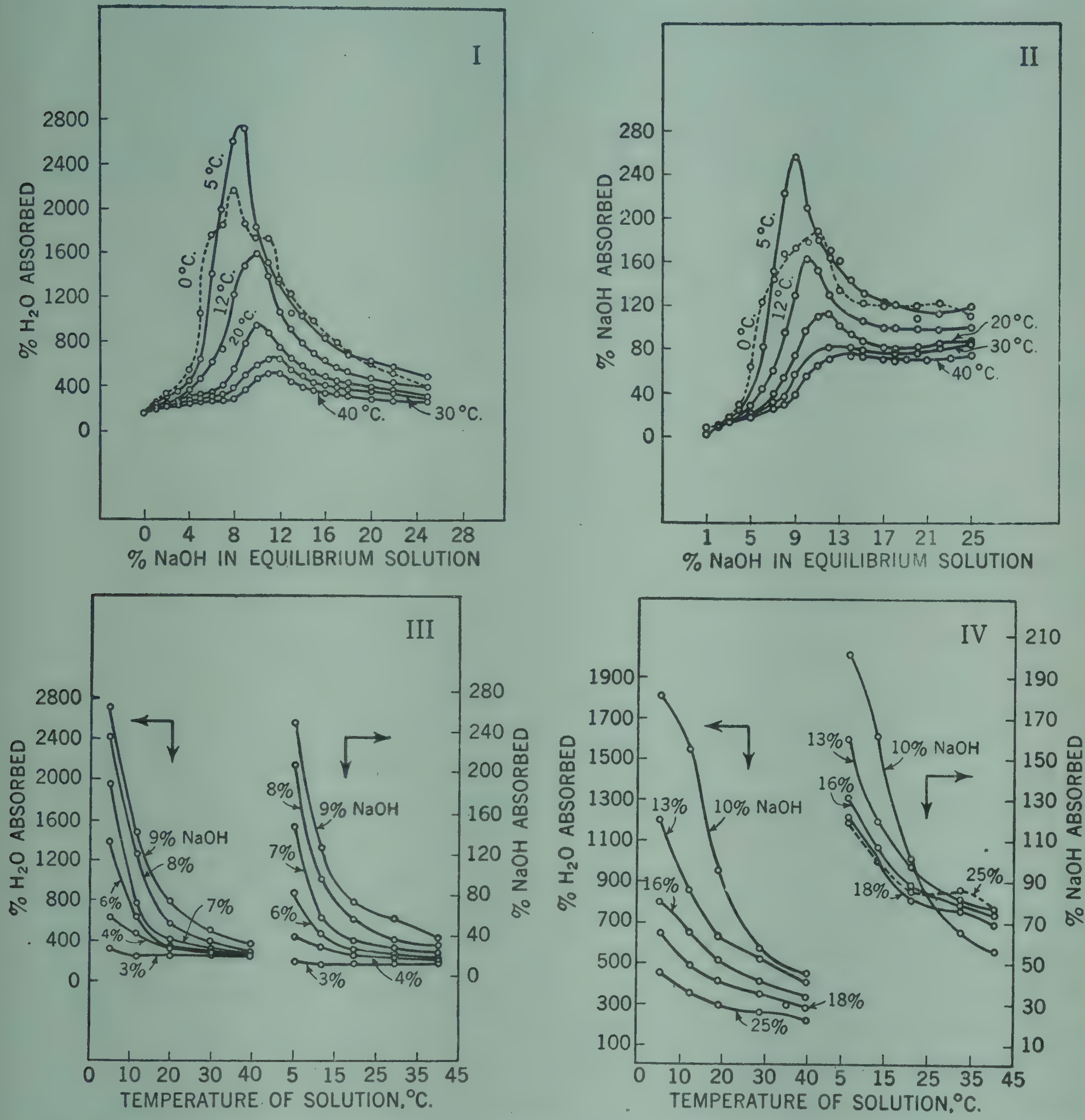

Fig. 35. Effects of temperature and concentration on total alkali and water absorbed by regenerated cellulose (Beadle and Stevens[20]).

are not similar, and this has been taken to mean that preferential absorption or chemical reaction occurs.

Neale[21] also employed the blotting method with small pieces of regenerated cellulose sheeting. His results (recalculated and graphically pre-

[21] S. M. Neale, *J. Textile Inst.*, **20**, T373 (1929); **21**, T225 (1930); **22**, T320, T349 (1931).

sented by Bancroft and Calkin) give the total quantities of sodium hydroxide and water absorbed from solutions of varying concentrations. The maximum water absorption (600%) occurs at about 12% alkali concentration (Fig. 36). On close study it is found that, if the amounts of alkali preferentially absorbed as indicated by the Vieweg change-in-titer curve (curve 2) are deducted from the total absorption (curve 1), the remaining quantities of alkali and water are present in the cellulose in almost exactly the same proportions as in the mother liquors. The differences in total absorption may be assumed, therefore, to represent mainly differences in the degree of swelling.

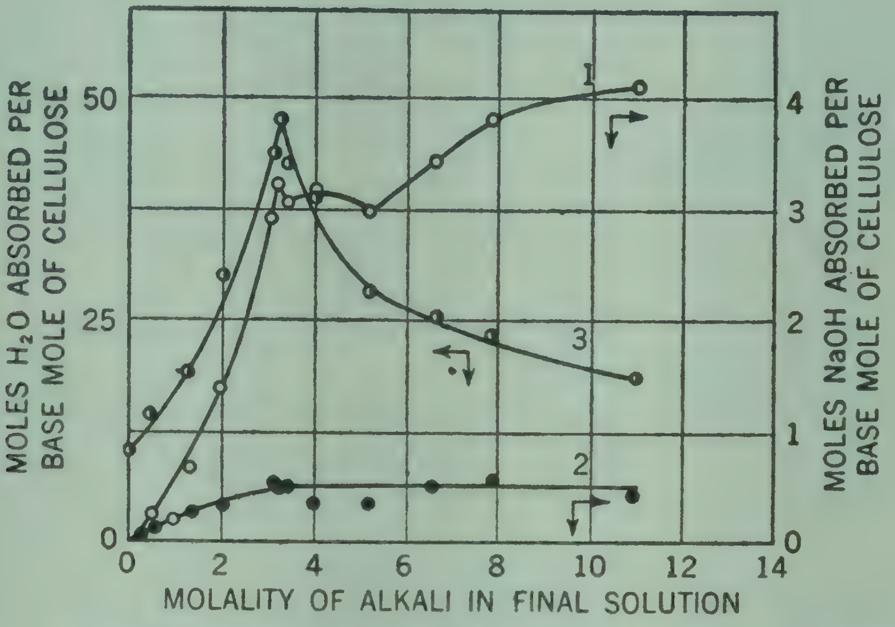

Fig. 36. NaOH and H_2O absorbed by cellophane at 25°C. (Neale's data recalculated by Bancroft and Calkin[11]). Curves: 1, total alkali absorbed; 2, preferentially absorbed alkali; 3, water absorbed.

Leighton[14] tried to determine the alkali absorbed by cellulose by using a centrifuge to remove excess alkali. The values he obtained produced a smooth absorption curve, and he concluded that no compound formation takes place. Similar conclusions were reached by Coward and Spencer,[22] and Bancroft and Calkin[11] who also used the centrifuge method. The last workers used an indirect method for determining the point at which all surface liquid was lost. Samples of the alkali cellulose were analyzed after various centrifuging intervals. The time required to remove surface liquid was assumed to be that at which no further change took place in the ratio of caustic to water leaving the cellulose.

Champetier[23,23a] has used a somewhat different method in which the alkali celluloses, instead of the centrifuged liquors, were analyzed after progressive centrifuging or pressing. The quantity of preferentially absorbed alkali (Fig. 37) was obtained by plotting the ratios of alkali-to-cellulose against water-to-cellulose and extrapolating to the zero axis for water. Champetier concluded that cellulose may form four stoichiometric compounds with either sodium or potassium hydroxides. No evidence of compound formation with lithium hydroxide was found. Probably the most serious objection that can be made to Champetier's method is that the extrapolations involved are large and the likelihood of error fairly great.

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[22] H. F. Coward and L. Spencer, *J. Textile Inst.*, **14**, T28, T32 (1923).

[23] G. Champetier, *Ann. chim.*, **20**, 5 (1933).

[23a] G. Champetier and K. Ashar, *Makromol. Chem.*, **6**, 85 (1951).

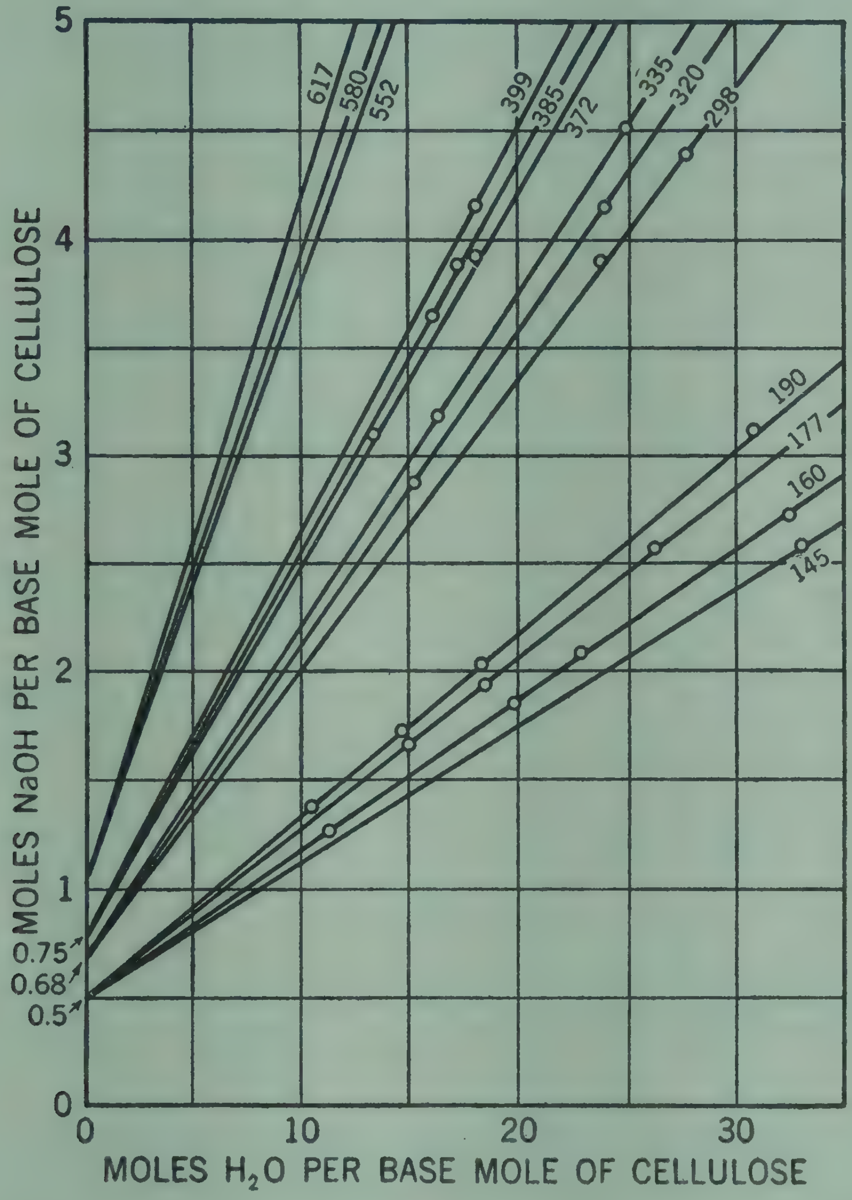

Fig. 37. Changes in the composition of the residues obtained by centrifuging to different degrees the alkali celluloses produced in NaOH solutions of various concentrations (Champetier[23]). The numbers on the curves represent the grams of alkali per liter.

(4) *The Neutral Salt Method*

Still another method used to study the formation of alkali cellulose has been to add a neutral salt such as sodium chloride to the alkaline treating solution. This method, originally used by Schwarzkopf,[24] is based on the assumption that if no salt is absorbed by the cellulose it should be possible to calculate the amount of water taken up by analyzing the mother liquor for chlorine before and after coming in contact with cellulose. Sharkov,[25] who also used this method, investigated its validity and concluded that it produced reasonable results provided the concentration of salt was low (1% or under). Bancroft and Calkin,[11] on the other hand, rejected the method as unsound, but their conclusion was based on the use of fairly concentrated salt solution.

Sharkov[25] and Saito[7] used the neutral salt method in conjunction with the Vieweg change-in-titer method to investigate the action of not only sodium hydroxide but lithium and potassium hydroxides as well. The data obtained do not agree absolutely but the general conclusions reached are similar.

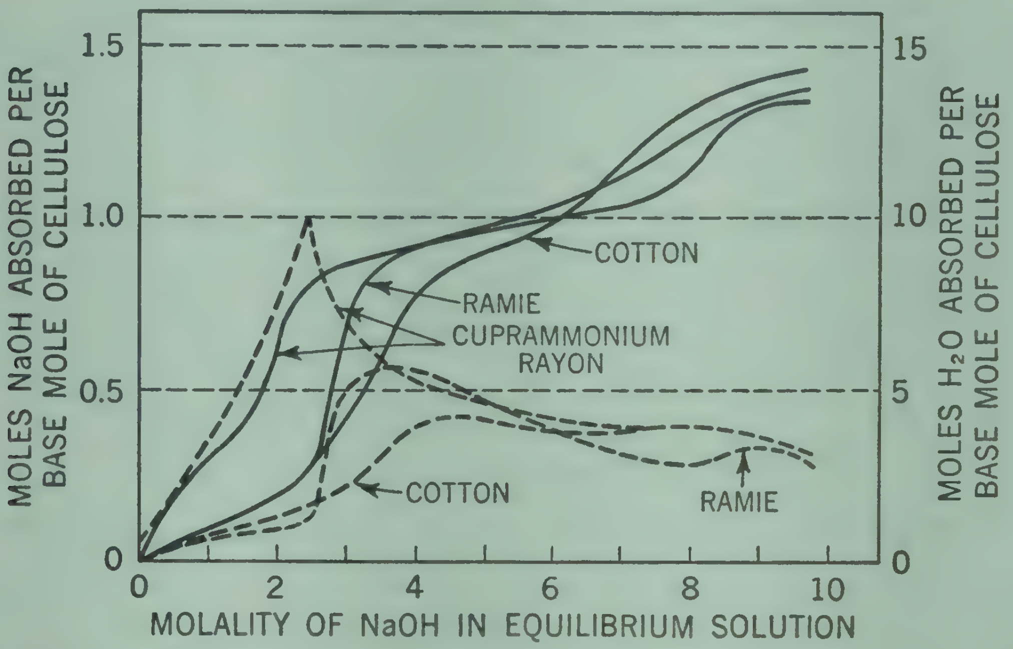

Fig. 38. Minimum true absorption of NaOH and H_2O by different cellulose fibers at 20°C. (Saito[7]). —— Minimum NaOH absorption; - - - - - minimum H_2O absorption.

Both Sharkov and Saito studied more than one cellulose and more than one alkali. Figure 38 shows data by Saito indicating that with sodium hydroxide there is a sharp increase in the amount of alkali absorbed by cellulose in the range of 2 to 4 *N* NaOH. Within this range, the amounts of sodium hydroxide absorbed vary considerably with the type of cellulose. Regenerated cellulose begins to absorb alkali strongly from solutions as weak as 2 *N*, similar absorption with ramie begins at about 3 *N*, and that for cotton at about 4 *N*. Between 4 and 6 *N* NaOH the absorption of alkali increases only very slightly, but above 6 N the increase occurs again. Saito showed that, for the celluloses investigated, the absorption taking place in 6 N alkali is independent of the type of cellulose used and is approximately 1 mole of alkali per mole of cellulose. In the case of water absorption, the amount for each cellulose passes through a maximum, but the absorption of water by regenerated cellulose at the maximum is more than twice that reached by cotton.

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[24] O. Schwarzkopf, *Z. Elektrochem.*, **38**, 353 (1932).

[25] V. I. Sharkov, *Iskusstvennoe Volokno*, **2**, 2 (1931).

On comparing the various methods for determining the absorption of alkali and water by cellulose it is interesting to note that they do not all give the same total (alkali + water) absorption. The neutral salt method, for example, produces only about half the absorption shown by either the blotting or centrifuge methods. This difference may be explained if cellulose, in the form of films or fibers, can be assumed to have a porous structure capable of holding relatively large amounts of mother liquor which by the blotting method would be included along with any liquor more intimately associated with the cellulose itself. Presumably the same would not be true for water absorption determined by the neutral salt method, and one should therefore expect to obtain lower values by this method.

(c) SWELLING OF ALKALI CELLULOSE

The physical swelling phenomena which all celluloses undergo when treated with a solution of an alkali hydroxide have as much theoretical interest and probably are more important practically than the purely chemical aspects of the changes involved in the formation of alkali cellulose. The two phenomena, chemical and physical, appear to be so completely interdependent that one cannot properly be considered without the other.

Mercer, in his study of the changes produced in cotton on treating with alkalies, observed generally the effects which swelling had on hygroscopicity, tensile strength, and dye affinity of the washed yarn. Crum,[26] in 1863, was the first to attempt a quantitative examination of the swollen condition of these fibers by measuring the cross section and determining the longitudinal shrinkage of cotton fibers. Crum also introduced the use of the microscope as a tool for studying swelling and described in detail how the fibers lose their flat, ribbon-like form and assume a nearly cylindrical appearance.

On the basis of modern concepts concerning the fine structure of cellulose, changes in length and diameter of the fiber depend on the fact that the network of cellulose chains and crystallites is most highly oriented in the direction of the fiber axis. The alkali solution, entering the network, pushes the units apart and loosens interconnecting secondary bonds, thus allowing the structure to assume a less oriented condition. However, the rupture of the secondary bonds is probably incomplete, so that the structure is still held together at certain points, and the shape of the fiber must change anisotropically, that is, more in one direction than in the other.

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[26] W. Crum, *J. Chem. Soc.*, **16**, 404 (1863).

Swelling differences observed in caustic solutions of varying concentrations can perhaps best be explained on the basis that penetration of alkali can be either inter- or intra-crystalline as first pointed out by Katz.[27] Since x-ray evidence indicates no change in spacing between individual cellulose chains when cellulose is brought into contact with solutions of caustic soda below 12% concentration, it may be assumed that in these solutions swelling takes place almost entirely between the crystallites. In solutions above 12% caustic soda concentration, the swelling process changes to the intracrystalline type, since alkali is preferentially absorbed or combined with the cellulose and a definite change occurs in the crystal lattice as determined by x-rays.

In addition to the important factors of solution concentration and temperature, already mentioned as influencing the degree of swelling and alkali absorption, the following variables may also be considered when cellulose is treated with a solution of an alkali: (1) the nature of the cellulose, (2) the time of contact, (3) hysteresis and equilibrium, (4) changes in solvent, and (5) presence of salts.

Purified cotton or ramie cellulose is less readily swollen by alkalies than is either mercerized or regenerated cellulose. Wood pulps usually occupy an intermediate position. The differences in ability to swell appear to be associated with the degree of orientation and crystallinity of the cellulose chain molecules and micellar aggregates composing the various cellulose structures. In addition, one must also consider the previous history of the sample, such as treatments with hydrolyzing or swelling agents. To illustrate, Figure 38 shows typical data covering the swelling effects produced by different concentrations of sodium hydroxide on ramie, cotton, and regenerated cellulose. It will be seen that the regenerated cellulose both reaches a maximum in swelling at a lower concentration of alkali and swells much more highly than either of the native celluloses. The conclusion may be drawn that the ease and degree of swelling increase with diminishing structural organization of the cellulose.

Heuser and Niethammer[13] have reported that both hydrocellulose and oxycellulose show an increase in degree of swelling and alkali absorption over the original cellulose. Neale[21] also studied the effects of alkali on ese degraded forms of cellulose but showed that, if these modified forms cellulose are treated with hot dilute alkali, they lose their increased sensi- vity toward swelling and alkali absorption and again behave as normal llulose. The latter result is due, presumably, to removal of degraded elluloses present in the hydrocellulose or oxycellulose.

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[27] J. R. Katz, *Physik. Z.*, 25, 321 (1924).

The time of exposure to alkali is not a critical factor in the swelling of ellulose provided the cellulose is in the form of loose fibers or thin sheets. Jnder most conditions, mercerization and swelling take place almost in- tantaneously, but this is not necessarily true in the commercial viscose rocess where relatively thick sheets of pulp are generally used. Under he latter conditions, air may be entrapped between the fibers in the sheets, nd it is important that it be expelled in order to obtain rapid and uniform welling. In some cases, particularly in the mercerization of unscoured otton fibers or highly purified wood pulps, the use of certain surface- ctive agents has been proposed to promote better wetting of the cellulose. Various mixtures of phenolic and hydroxy aliphatic compounds, several of which are described in the patent literature, are useful for this purpose.

(1) *Neale's Theory of Swelling*

Among the theories which have been advanced to explain swelling, one f the most interesting is that suggested by Katz[28] and Pauli and Valko,[29] nd worked out by Neale.[21] According to this theory, the action of alkali n cellulose can best be represented as an osmotic effect. This is based on he assumption that cellulose may be regarded as a weak monobasic acid which forms a sodium salt approximately according to the laws of mass ction. The reasons why a more exact adherence to the mass action laws s not obtained are three. First, the reacting system is not homogeneous ecause of the variation in hydroxyl availability through the cellulose fiber. Second, the cellulose molecule, being a high polymer, is polybasic, and it ontains several different types of acid structures. Third, the alkalies sed are in extremely high concentration, and the activities of the ions are o longer even roughly proportional to their concentrations. To help xplain this theory Neale gives the following diagram:

$$\begin{array}{ccccc} \mathrm{H} & \mathrm{Na}^+ & \mathrm{H} & \mathrm{Na}^+ & \mathrm{Na}^+ \\ \mathrm{A} & \mathrm{A}^- & \mathrm{A} & \mathrm{A}^- & \mathrm{A}^- \end{array}$$

n which A is the negatively charged unit or radical corresponding to each cid hydrogen atom. In dilute sodium hydroxide solution certain of these hydrogens are replaced by sodium. The cations may be imagined as constantly moving within the network from point to point, replacing and being replaced by others, so that under given conditions a state of dynamic equilibrium is reached between sodium ion, hydrogen ion, or undissociated cellulose hydroxyl groups. It is believed that a similar type of equilibrium could exist between sodium hydroxide and a sodium hydroxide–cellulose complex. Excess alkali may be thought of as diffusing into the cellulose in an amount determined by Donnan's thermodynamic equation for membrane equilibrium. The resulting unequal distribution of ions causes osmosis, imbibition of water, and swelling of the cellulose until the osmotic pressure is balanced by forces arising from the cohesion of the gel. On washing with water, the cellulose sodium salt is hydrolyzed, the osmotic pressure falls, and the cellulose is recovered unchanged chemically but distorted physically by an amount depending upon the maximum osmotic pressure reached. The value 1.84×10^{-14} was determined as the ionization constant of the regenerated cellulose, and Neale calculated a theoretical osmotic pressure curve which was found to agree fairly well with the experimentally determined water absorption curve (Fig. 39). Neale, on the basis of this theory, was able to account for the greater swelling of cellulose in alkali solutions of intermediate concentration and also to explain why swelling is greater and the optimum concentration producing it is lower for lower temperatures.

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[28] J. R. Katz, *Micellartheorie und Quellung der Cellulose,* in K. Hess, *Die Chemie der ellulose,* Akadem. Verlagsgesellschaft, Leipzig, 1928.

[29] W. Pauli and E. Valko, *Elektrochemie der Kolloide,* J. Springer, Vienna, 1929.

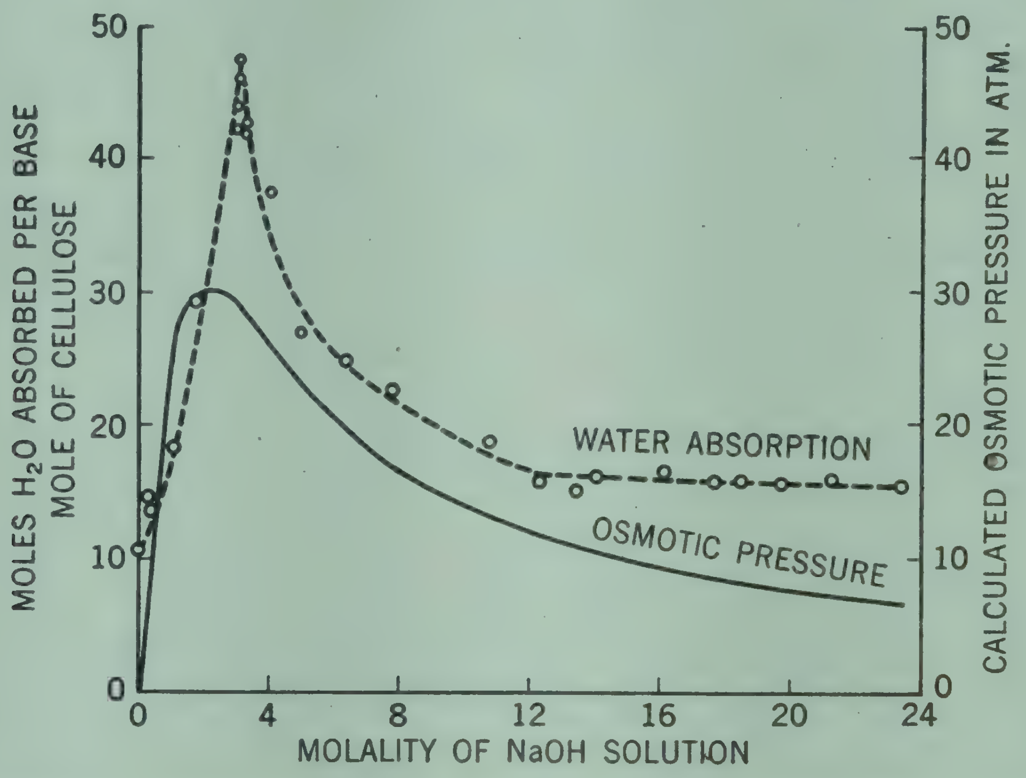

Fig. 39. Osmotic pressure and water absorption of cellulose film (cellophane) from NaOH solutions of different concentrations (Neale[21]).

If cellulose is treated with a concentrated solution of alkali and then nmersed in water or dilute alkali, it undergoes a transient swelling which s much greater than that produced by direct treatment with dilute alkali. Neale explained this phenomenon on the basis that a sudden rise in osmotic pressure causes imbibition of water and rapid swelling of the solid phase.

(2) *Other Theories of Swelling*

Besides the theory of Neale, several other mechanisms have been suggested to explain the swelling of cellulose in alkali, but in general these have not been accepted by all workers in the field.

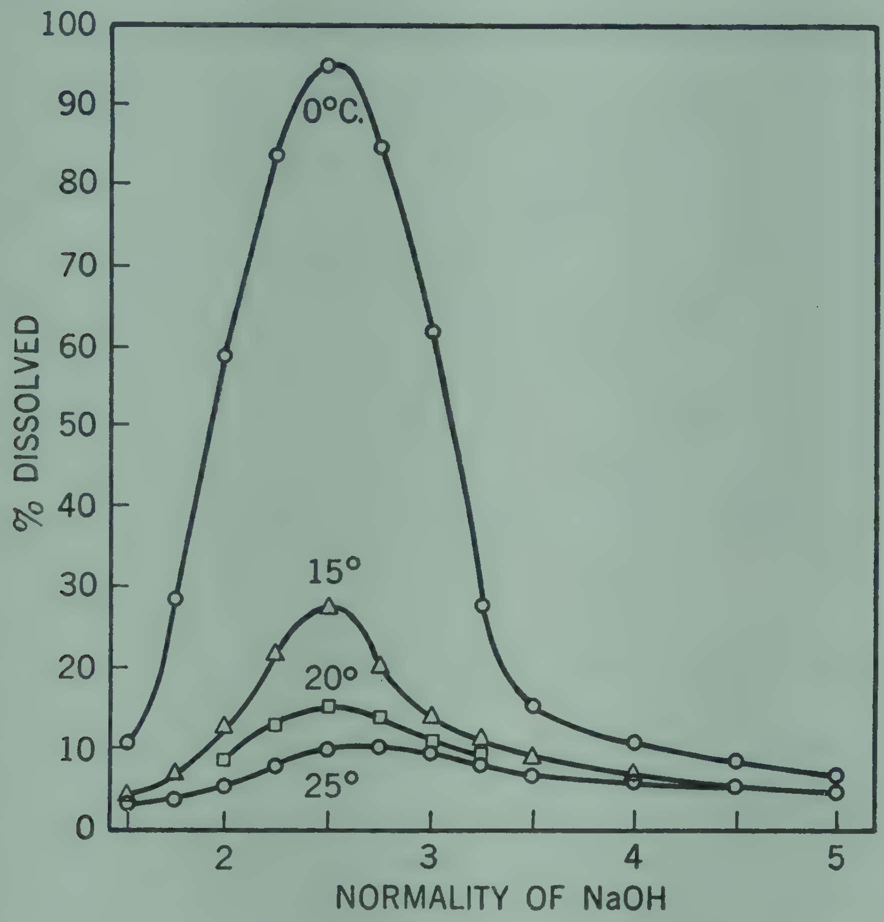

Fig. 40. Solubility of cellophane in NaOH solutions at various temperatures (Davidson[30]).

One of these theories states that the swelling is a result of osmotic pressure, but that the pressure is due to dissolved cellulose molecules in the fiber. Davidson[30,31] demonstrated that solubility, like swelling, passes through a maximum and that both of these maxima occur at approximately the same alkali concentration. In Figure 40 the solubility of cellophane at various temperatures is shown as a function of sodium hydroxide concentration. The solubility is expressed as the ratio of dissolved to

[30] G. F. Davidson, *J. Textile Inst.*, **27**, T112 (1936).

[31] G. F. Davidson, *J. Textile Inst.*, **25**, T174 (1934).

undissolved material in a large excess of aqueous alkali. The solubility in sodium hydroxide is much greater than in potassium hydroxide and this corresponds also to the behavior observed with the swelling.

Another explanation is that the swelling is caused by hydration; that is, by the cohesive forces between the alkali cellulose compound and the water molecules. With increasing concentration of alkali hydroxide, there is an increasing competition between the free Na^+ and OH^- ions and the alkali cellulose for the water molecules; consequently, the hydration of the alkali cellulose compound diminishes. It is interesting to note in this connection that, according to Hess and his collaborators,[32] the crystallized alkali cellulose contains water of hydration. At the lower alkali concentrations, the stable alkali cellulose I contains 3 moles of water per $C_6H_{10}O_5$ compared with 1 mole of water per $C_6H_{10}O_5$ in the alkali cellulose II, which is stable only at higher alkali concentrations. However, the swelling, especially that of the regenerated cellulose, is too extensive to be attributed solely to the amount of water of crystallization.

A third explanation is that the swelling is caused by the electrostatic repulsion between the cellulose particles which, on account of the ionization of the alkali cellulose, possess an excess of negative charges. At higher alkali concentrations the free ions exert a screening effect on the electrostatic repulsion. This is, of course, associated with the reduction of osmotic effect considered in the discussion of the theory of Neale.

(3) *Heat of Swelling*

When cellulose is treated with an alkali solution of sufficient strength to produce swelling, heat is developed. Several investigators[33,34] have attempted to measure the heat liberated with the object of relating the heat of reaction with the degree of swelling and compound formation. For caustic solutions up to 10 M, the results have been in fairly good agreement for cotton cellulose and indicate that the heat of mercerization increases with the strength of the solution, but is not proportional to it. Barratt and Lewis[35] as well as Neale[21] obtained a definite deflection between 3 and 4 M concentration indicating a sharp rise in the heat produced (Fig. 41). It will be recognized that this range of alkali concentration coincides perfectly with that shown to produce mercerization and formation of an alkali cellu-

[32] H. Sobue, H. Kiessig, and K. Hess, *Z. physik. Chem.*, **B43**, 309 (1939).

[33] I. Okamura, *Naturwissenschaften*, **21**, 393 (1933).

[34] J. L. Morrison, W. B. Campbell, and O. Maass, *Can. J. Research*, **B18**, 168 (1940).

[35] T. Barratt and J. W. Lewis, *J. Textile Inst.*, **13**, T113 (1922).

ose compound. It is also in this range that the x-ray structure has been observed to change markedly. Barratt and Lewis[35] further found that a less marked increase in heat evolved was obtained above 10 *M* concentration of alkali, but Neale[21] did not confirm this and has stated that the heat evolved continues to rise rapidly for solutions containing up to 20 *M* concentration of sodium hydroxide. Neale also found that the curve representing heat evolved by regenerated cellulose on swelling was different from that found

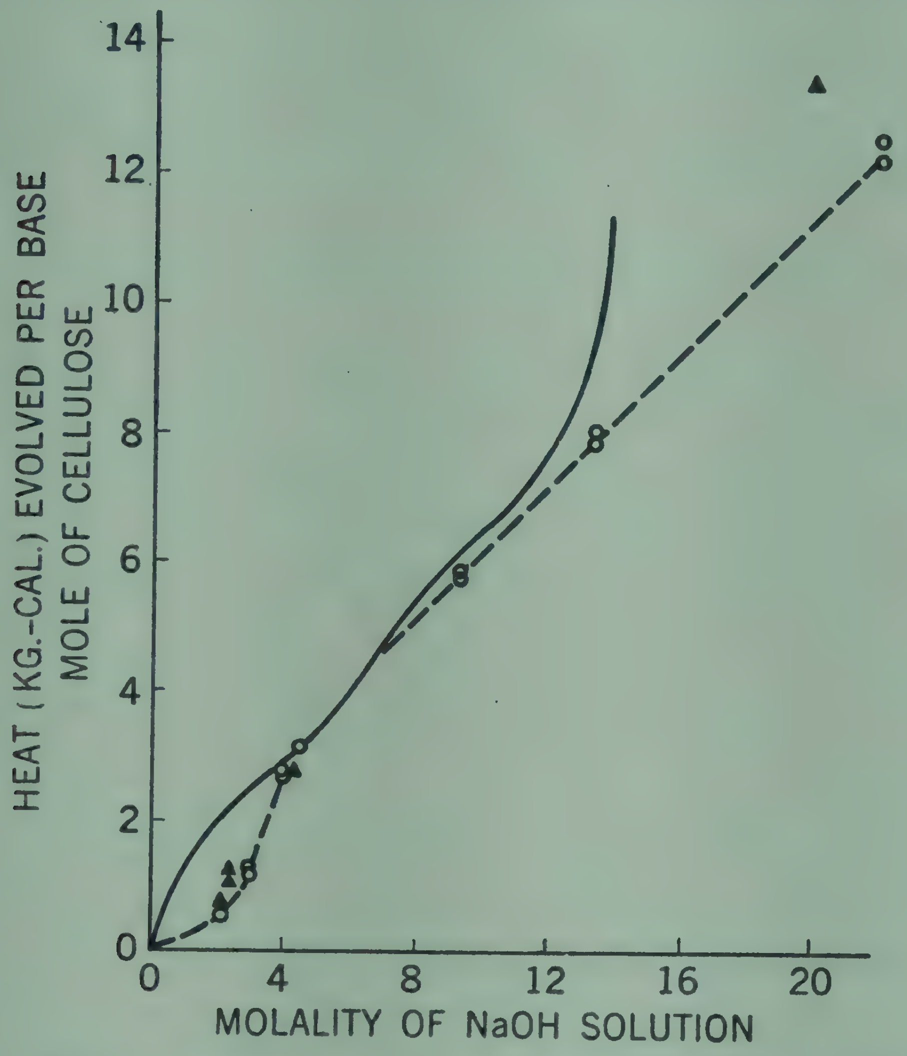

Fig. 41. Heat evolved on treating various celluloses with alkali (Neale[21]).

—— Viscose rayon.
○ Cotton, soda-boiled.
▲ Cotton, soda-boiled and mercerized.

for cotton. With the regenerated cellulose, the initial steep rise in the curve was obtained in solutions of less than 2 *M* concentration as compared with 3 to 4 *M* for cotton. This was explained by the assumption of an “accessibility” factor which was considered to be greater for the relatively unorganized structure of regenerated cellulose than for the highly organized structure in cotton.

Neale's[21] conclusions have been criticized by Bancroft[11] on the basis that “heat of reaction” may just as well be called “heat of absorption,” since the thermal data obtained could be said to fit one as well as the other. It seems possible that these differences in points of view might be reconciled if it were assumed that, at the higher concentrations of alkali, the heat evolved can be due to both absorption and chemical combination while at lower concentrations, where no changes in x-ray diagram can be detected, the heat evolved is due to absorption only. As is the case elsewhere in this book, it appears proper to re-emphasize the fact that the magnitude of the forces binding sodium hydroxide to cellulose hydroxyls does not vary along the chain, but that reaction with the disorganized portions occurs at a lower concentration due to their greater availability. This portion of the reaction, of course, does not affect the x-ray diagram.

(4) *Effects of Added Solvent on Swelling*

The addition of alcohol, alone or in combination with water, has been used by several investigators as a means of determining the nature of alkali cellulose. Both Vieweg[12] and d'Ans and Jäger[15] found that for a given concentration of alkali the apparent amount of sodium hydroxide taken up by cellulose as determined by the change-in-titer method increases with increase in the amount of alcohol added. Vieweg concluded that with alcohol present no chemical combination occurred between celluloses and caustic soda. d'Ans and Jäger (Fig. 42), however, obtained flat portions in the curves for 10% and 20% alcohol and showed that the absorption curves change position in relation to the alkali concentration and that the amounts of alkali absorbed at the inflection points in these curves are greater with increasing alcohol concentration. Bancroft and Calkin,[11] also using the change-in-titer method, found considerably more alkali absorbed from 95% alcohol than from an aqueous solution of the same alkali concentration. Champetier[35a] has reported that the rate of fixation of alkali is markedly faster in a water–ethyl alcohol mixture than in either water or ethyl alcohol alone. Also, Legrand and Grund[35b] found that the concentration of alcohol influences profoundly the relative proportions of alkali celluloses I and II which exist after equilibrium is reached. Beadle and Stevens,[20] using the blotting method, noted, on the other hand, that both the total sodium hydroxide and the water absorbed decreased on addition of absolute alcohol.

It is believed that a comprehensive explanation for these data might be found if it is remembered that cellulose takes up water readily, but absolute cohol slightly, if at all. Also, caustic soda is much less soluble in alcohol an in water, and, in the case of a caustic soda–alcohol–water system, e effective concentration of alkali in the water would be far greater than no alcohol were present. In such a system the apparent increase in the lkali taken up by the cellulose would be greater by the change-in-titer ethod of measurement, but, because of a decrease in swelling, the over-all bsorption of alkali as judged by the blotting method might actually be

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[35a] G. Champetier, C. Legrand, and G. Gombaud, *Compt. rend.*, **233**, 1602 (1951).

[35b] C. Legrand and A. Grund, *J. Polymer Sci.*, **9**, 527 (1952).

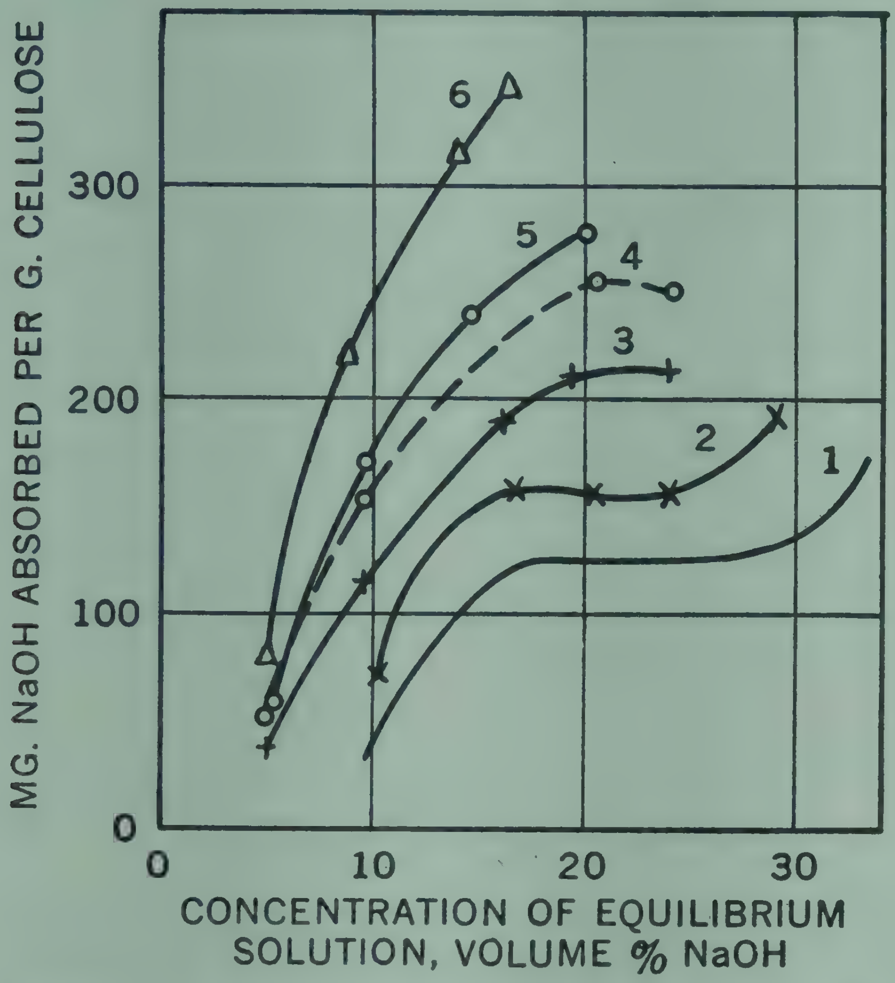

Fig. 42. NaOH preferentially absorbed by cellulose in the presence of alcohol (d'Ans and Jäger[15]). Curves: 1, 0% alcohol, 23°C.; 2, 10% alcohol, 23°C.; 3, 20% alcohol, 23°C.; 4, 30% alcohol, 23°C.; 5, 40% alcohol, 23°C.; 6, 20% alcohol, 2°C.

ess. Also, if the alkali cellulose were formed first and afterward treated ith alcohol, the water taken out of the cellulose by the alcohol might be xpected to carry out appreciable amounts of caustic soda, though any lkali preferentially absorbed should not be affected to the same extent.

(5) *Effects of Salts on Swelling*

Neutral salts, particularly sodium chloride, have been added to the cellu-se–caustic soda–water system with the object of influencing swelling nd the amount of alkali absorbed. The reported results again are not in complete agreement, but most investigators have found that for concentrations from 5 to 20%, sodium chloride decreases swelling but increases the amount of alkali absorbed by the cellulose. Schwarzkopf,[24] d'Ans and Jäger,[15] and others have claimed that sodium chloride is itself not absorbed by cellulose in the presence of alkali; and Schwarzkopf, as we have seen, used the presence of sodium chloride as a method for determining the amount of water absorbed. Saito[7] studied the effects produced on the amount of alkali absorbed by increasing the concentration of sodium chloride and found that, while the apparent absorption (change-in-titer method) increases gradually, the total absorption of alkali and water actually decreases slightly (Fig. 43). It is believed that these findings may be explained on the same general basis as has been used to explain the effects of alcohol on alkali cellulose.

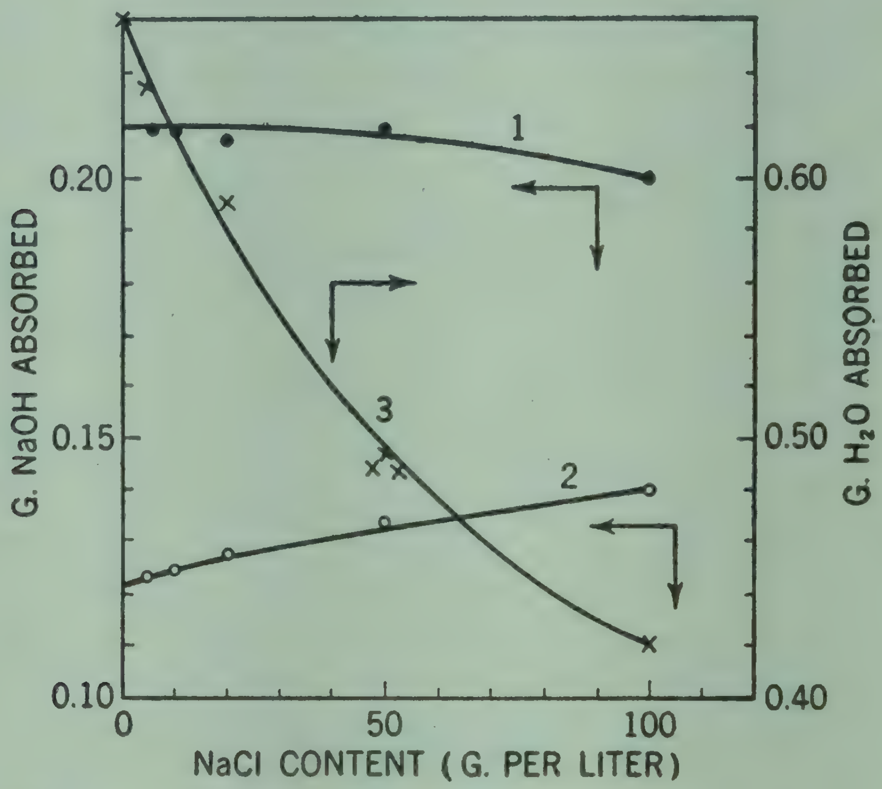

Fig. 43. Effects of NaCl on the total and preferential absorption of NaOH and total absorption of H_2O from NaOH solution (140 g. per liter) at 20° C. (Saito[7]). Curves: 1, minimum true NaOH absorption; 2, preferential NaOH absorption; 3, total absorption of water.

Joyner[36] studied the effects of potassium salts and concluded that potassium chloride has a more powerful effect than sodium chloride in influencing alkali absorption. Jimbo and coworkers[37] tested the effect of sodium chloride in the preparation of alkali cellulose for the viscose process. They concluded that small quantities, up to 2%, may exert a slight beneial influence on the properties of the regenerated yarns, but that higher ncentrations of salt cause difficulty in filtration, probably due to a reduction in the degree of swelling achieved during steeping.

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[36] R. A. Joyner, *J. Chem. Soc.*, **121,** 2395 (1922).

[37] S. Jimbo, T. Takazawa, and K. Tanaka, *J. Soc. Chem. Ind., Japan,* **37,** B395 (1934).

(d) METAL HYDROXIDES OTHER THAN SODIUM HYDROXIDE

Although most of the work covering the action of alkalies on cellulose as been concerned with sodium hydroxide, some attention has also been ven to the hydroxides of the other alkali metals.

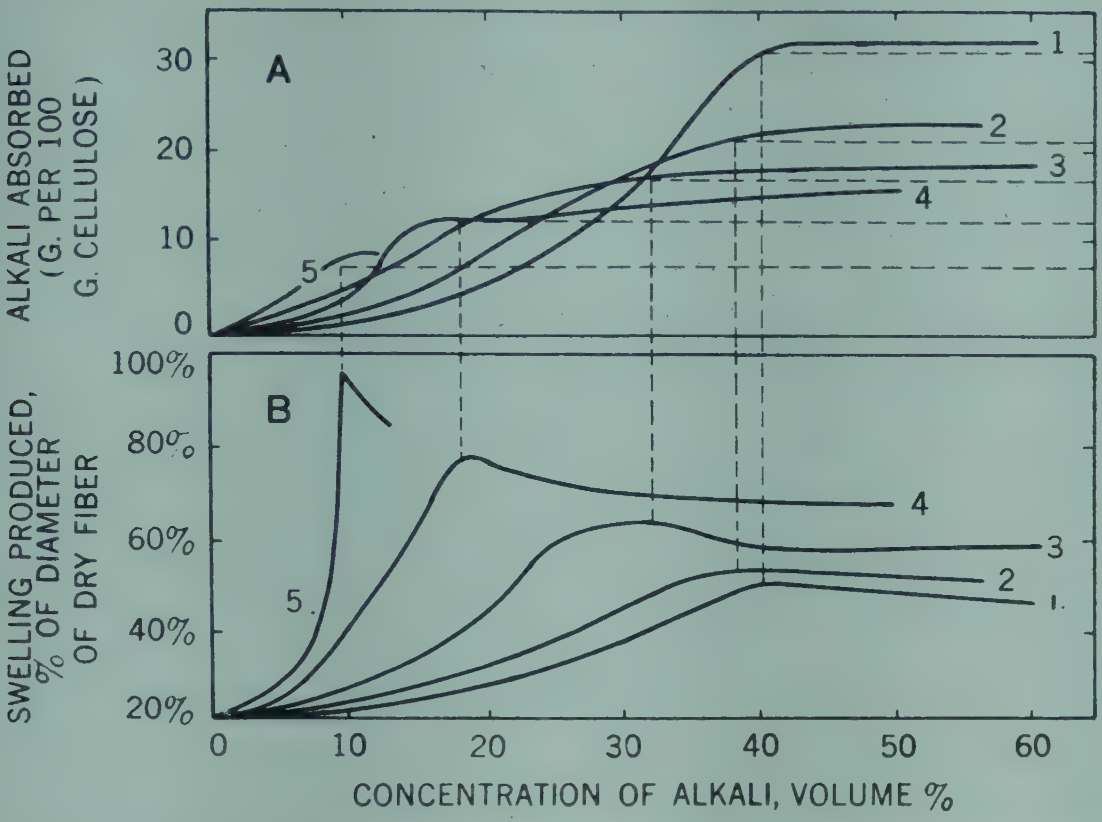

Fig. 44. Comparison of (A) the alkali absorbed by and (B) the swelling produced cellulose on treatment with solutions of various alkali metal hydroxides (Heuser nd Bartunek[38]).

Curve	Alkali	Concentration of maximum swelling	Pseudostoichiometric ratio
1	CsOH	40%	$(C_6H_{10}O_5)_3 \cdot CsOH$
2	RbOH	38%	$(C_6H_{10}O_5)_3 \cdot RbOH$
3	KOH	32%	$(C_6H_{10}O_5)_2 \cdot KOH$
4	NaOH	18%	$(C_6H_{10}O_5)_2 \cdot NaOH$
5	LiOH	9.5%	$(C_6H_{10}O_5)_2 \cdot LiOH$

Heuser and Bartunek,[38] using the hydroxides of lithium, sodium, po-assium, rubidium, and cesium, found that each produces an absorption urve by the change-in-titer method which contains a break interpreted s indicating the formation of a definite compound with the cellulose (Fig. 4A). In the case of lithium and potassium hydroxides, the compounds are strictly analogous to that formed with sodium hydroxide and may therefore be represented by the general formula $(C_6H_{10}O_5)_2 \cdot MOH$ where M is the alkali metal. With rubidium and cesium hydroxides, the indicated compounds contain 3 moles of cellulose for each mole of hydroxide and would therefore be represented by $(C_6H_{10}O_5)_3 \cdot MOH$. The concentrations of alkali in solution required for the formation of these compounds increase in the same order as the atomic weights of the alkali metals, which is: $Li < Na < K < Rb < Cs$. It is also to be noted that for the first three hydroxides the molar concentration at which the break in the absorption curve occurs is almost identical, although the per cent concentration increases.

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[38] E. Heuser and R. Bartunek, *Cellulosechemie*, **6**, 19 (1925).

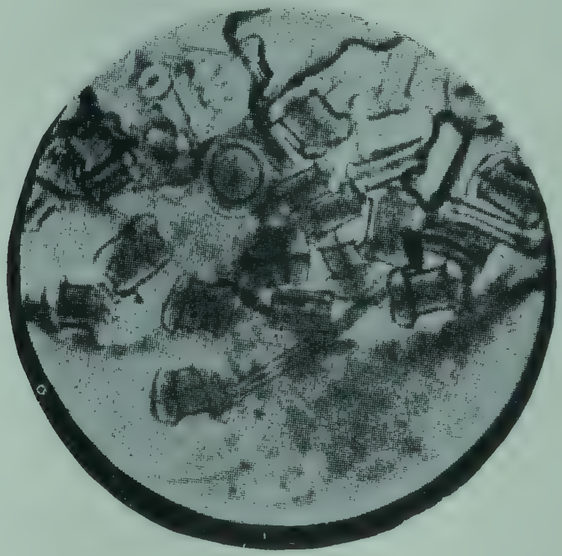


Fig. 45. Photograph showing the "dumbbell-like" swelling of microscopic sections of cotton fibers in mercerizing solutions (Willows and Alexander[39]).

The degree of swelling, determined microscopically by observations on the cross section of the treated fiber, has also been studied for the various metal hydroxides. However, the examination of transverse sections can lead to errors on account of the so-called "dumbbell-like" swelling, which was first observed by Willows and Alexander[39] (Fig. 45). This occurs with cotton at the mercerizing concentration due to the extrusion of the cellulose from the ends of the section during the swelling process. More reliable results can be obtained by measuring the width of the whole fiber.

Heuser and Bartunek (Fig. 44B) found that, for each hydroxide, swelling of scoured cotton passes through a maximum at a concentration of alkali which corresponds closely with that producing the break in the change-in-titer curve. The degrees of swelling at the maxima for the various alkalies

[39] R. S. Willows and A. C. Alexander, *J. Textile Inst.*, **13,** T237 (1922).

are in the same relative order as the degrees of hydration of the respective metal ions. The ions of lowest atomic volume are associated with the greatest number of water molecules, and in solutions of the various hydroxides in which the $MOH:H_2O$ ratios are the same as those corresponding to the fully hydrated ions, maximum swelling occurs. Both hydration of these hydroxides and swelling of alkali cellulose increase with decrease in temperature.

Saito[7] studied the absorption of alkali and water by cellulose from solutions of lithium, sodium, and potassium hydroxides by using the alkali–neutral salt method. The data obtained agree at least qualitatively with those found by the change-in-titer method and indicate breaks in the curves for preferentially absorbed alkali at about the same molar concentrations. Swelling at the maxima was found to decrease with increase in the molecular weight of the alkali. Saito[7] also studied effects obtained through the use of mixtures of these alkalies, taken two at a time, the results being of interest chiefly because the values found did not always lie intermediate between the values produced by either alkali alone. Mixtures of lithium and potassium hydroxides, for example, produce swelling values which pass through a maximum at a ratio of 1:1. Mixtures of lithium and sodium hydroxides, on the other hand, produce values showing a minimum at approximately a 1:1 ratio. The only mixtures behaving normally are those containing sodium and potassium hydroxides, for which all swelling values are intermediate between those characteristic of each alkali alone.

(e) EFFECTS PRODUCED BY DILUTION OR CONCENTRATION OF ALKALI SOLUTIONS

The curve for alkali absorption determined by the change-in-titer method is not retraced exactly when a strong solution of alkali in contact with cellulose is diluted. In the case of cotton cellulose, for example, Bancroft and Calkin[11] found that dilution of a 5 *M* alkali solution gave values for alkali absorption which were considerably greater than those obtained either by direct treatment with solutions of equivalent concentrations or by progressively increasing the concentration of alkali in solution (Fig. 46). It has been similarly shown by Saito[7] that, with both ramie and cotton cellulose, progressively decreasing the concentration of alkali in solution produces a shift in the swelling maximum in the direction of lower alkali concentration (Fig. 47). The extent of the shift appears to be dependent on the initial concentration of the alkali used and, within limits, increases with this initial concentration. Evidence points, therefore, to the con-

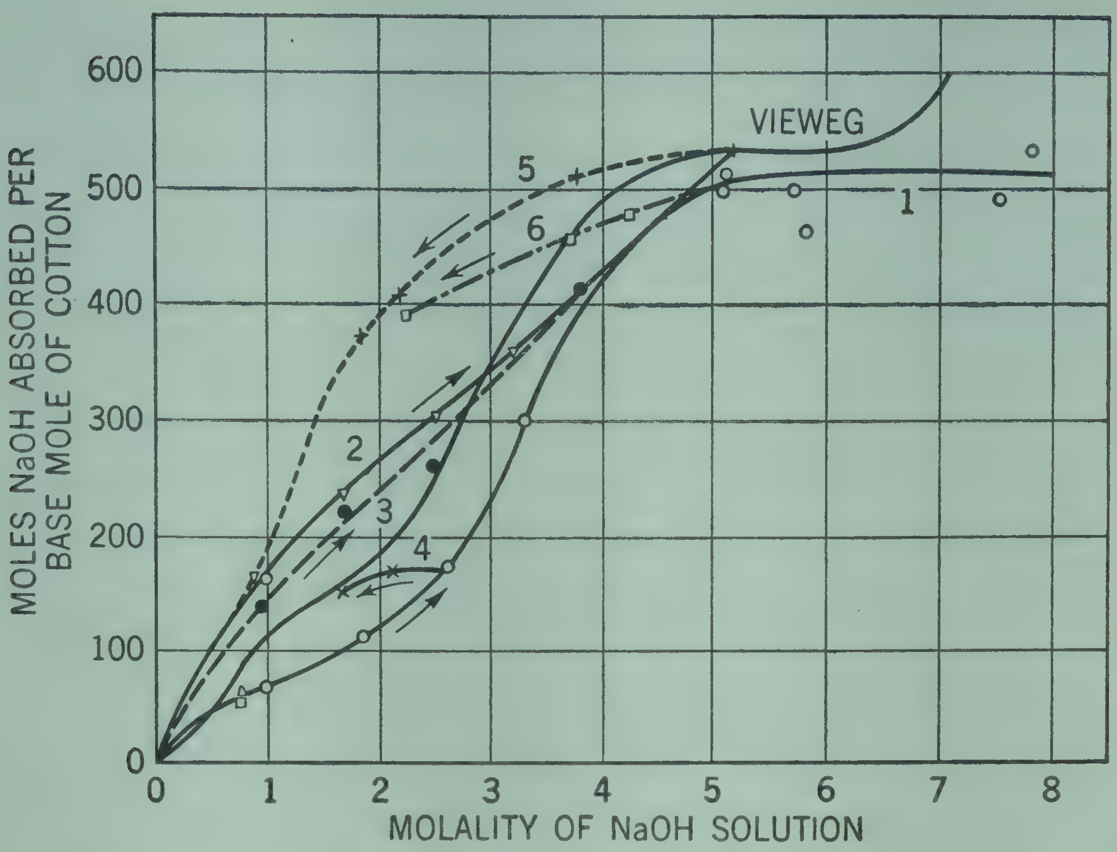


Fig. 46. Preferential absorption of alkali obtained on dilution and concentration of solutions of NaOH (Bancroft and Calkin[11]).

Curves

Concentration	Dilution
1, ○	4, ×
2, ▽	5, +
3, ●	6, □

Vieweg (no points)

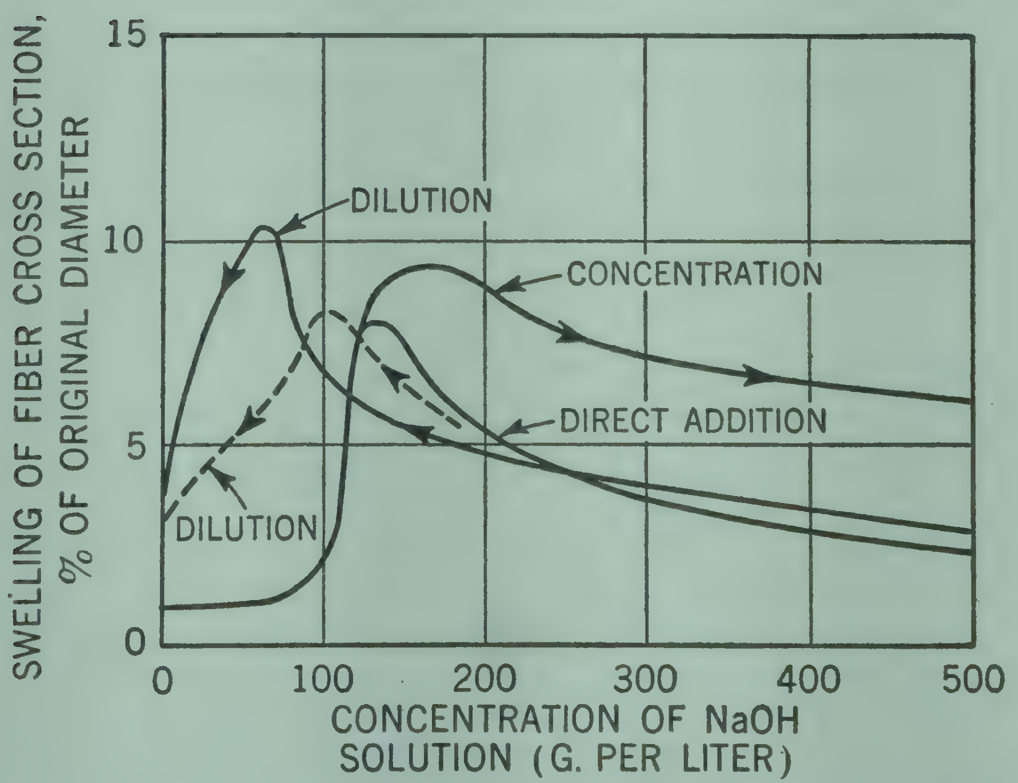


Fig. 47. Comparison of effects on the swelling of ramie cellulose obtained by dilution and concentration of solutions of NaOH (Saito[7]).

clusion that alkali absorption and swelling are both incompletely reversible phenomena, although the alkali can be entirely removed if the cellulose is washed thoroughly with water.

Saito[7] also obtained data for changes in swelling when the concentration of alkali is increased stepwise. Under such conditions fibers remain greatly swollen at the higher concentrations, although normally they are not so highly swollen if the cellulose is introduced directly. This investigator also studied the effects of varying the temperature of the alkali solution over the range 14–31°C. before and after adding cellulose. Swelling and alkali absorption data were obtained for conditions in which the cellulose was added directly to the solution at different temperatures, and for conditions in which the cellulose was put in contact with the alkali solution and the temperature subsequently either increased or decreased. From Figure 48 it is apparent that, if the cellulose is initially introduced into a cold solution of alkali, the amount of alkali absorbed is not changed

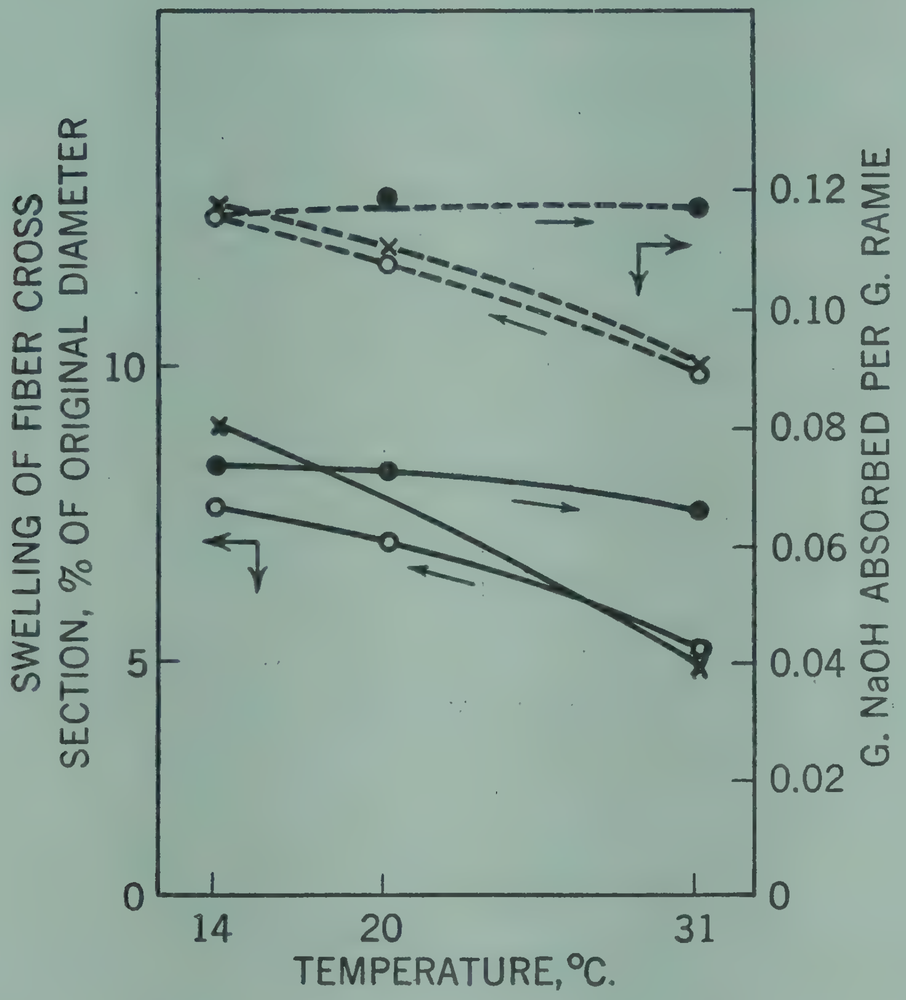


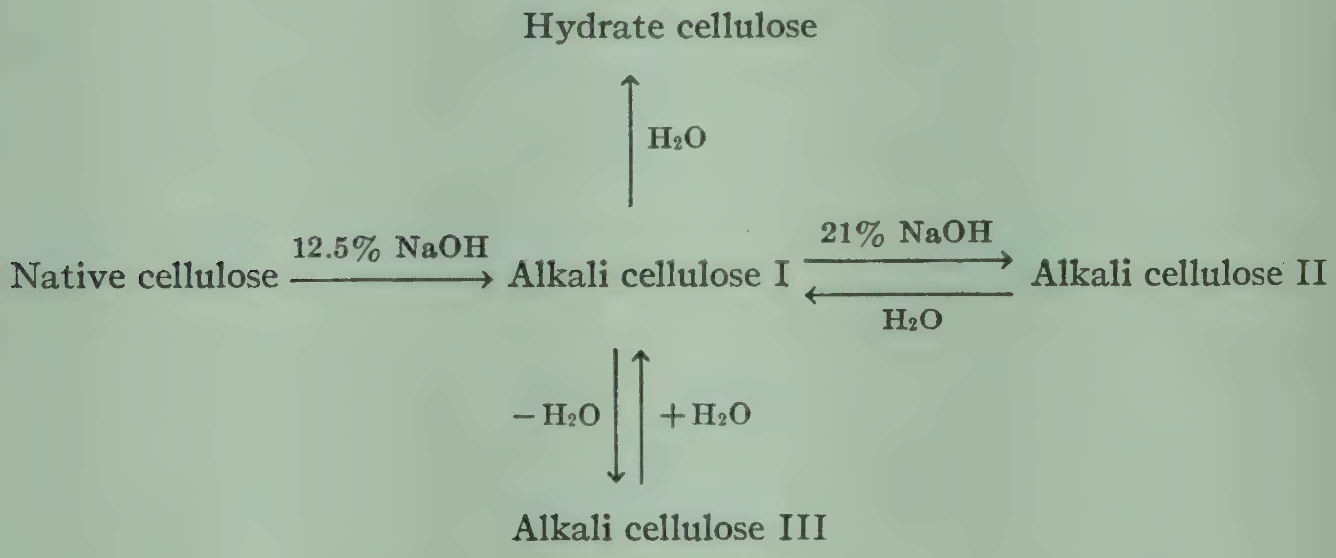
Fig. 48. Effects of temperature on swelling and alkali absorption of ramie cellulose in NaOH solutions (130 g. per liter) (Saito[7]).

○—Decreasing temperature.
●—Increasing temperature.
×—Direct introduction of cellulose.

appreciably by increasing the temperature, although this is not true if the cellulose is introduced at a higher temperature and the solution allowed to cool. To some degree the same relationships hold for swelling. These observations, in general, may be considered to confirm the nonreversible character of the swelling process.

(f) EXAMINATION OF ALKALI CELLULOSE BY X-RAYS

The application of x-rays to the study of alkali cellulose has been of tremendous value in helping to clarify questions regarding the nature of the material itself and the changes which take place when cellulose is treated with alkali solutions of different concentrations. Evidence supplied by Hess and Trogus,[40] von Susich and Wolff,[41] and others indicates that certain definite changes take place in the crystalline structure of cellulose when it is treated with sodium hydroxide solutions. The principal relationships found by these workers may be summarized by the following scheme:



The changes in crystal structure, while strongly suggesting the formation of definite compounds, do not occur sharply but show a gradual transition over a range of several per cent alkali. This, as already noted, agrees with observations made on the alkali absorbed by cellulose from caustic soda solutions of different concentrations. Alkali cellulose I as defined by x-ray studies may therefore be identified with the ordinary alkali cellulose obtained in 16–18% alkali, and alkali cellulose II is probably identical with the product of mercerization as normally carried out in the stronger alkali solutions used in the treatment of textiles. Alkali cellulose III is a third form obtained by dehydration of alkali cellulose I.

[40] K. Hess and C. Trogus, *Z. physik. Chem.*, **B4**, 321 (1929); **B11**, 381 (1930).

[41] G. von Susich and W. W. Wolff, *Z. physik, Chem.*, **B8**, 221 (1930).

More recently Neumann[42] found that if alkali cellulose I is made from a hydrated cellulose and the concentration of alkali in solution is gradually decreased, there is formed below about 6% alkali concentration a fourth modification in crystal structure, which he termed alkali cellulose IV. Following this, Schramek and Görg[43] found that, if alkali cellulose I derived from hydrate cellulose is treated with caustic soda of 25–28% concentration, it may be converted temporarily into still another crystal form which was termed alkali cellulose V. The latter is not stable, however, and on standing gradually reverts to alkali cellulose II. If the alkali concentration in contact with alkali cellulose II is then reduced, further changes occur as indicated by a gradual transition through alkali cellulose I and, below 6% alkali, to alkali cellulose IV. The relationships between alkali celluloses II, III, and V have been studied thermodynamically by K. Lauer,[43a] who determined the heats evolved on treating cotton and mercerized cotton with alkali solutions in the range 18.6–40.2% NaOH. The data obtained were explained on the basis of varying proportions of crystalline, semicrystalline and amorphous celluloses present. Sobue[44] has shown that at low temperatures where swelling is very high, two further compounds of cellulose and sodium hydroxide exist. These have been designated as alkali cellulose VI and alkali cellulose Q. Sobue has summarized the interrelationships of most of the known alkali cellulose compounds as revealed by x-ray methods (Fig. 49).

The importance of swelling in the formation of the various crystalline modifications of alkali cellulose detectable by x-rays is shown by the fact that if hydrate cellulose is used, the conversion to alkali cellulose I takes place at a lower concentration of alkali than is the case with native cellulose. Moreover, alkali cellulose I, made from hydrate cellulose, does not convert to alkali cellulose II in 20–25% NaOH but only in solutions more concentrated than 28% NaOH. Observed differences in the alkali concentration ranges which give rise to a given lattice structure under conditions of increasing caustic concentration, as opposed to decreasing caustic concentration, are also most readily explained on the basis of swelling.

Further evidence of the importance of swelling on change in crystal structure is the fact that alkali cellulose I is not obtained in water-free solutions of sodium hydroxide–methanol which are known to be poor swelling agents for cellulose. Tension, which is also known to affect swelling, has been found to affect changes in the x-ray diffraction diagram. On the basis of this relationship, Hess and Trogus[40] were able to show that ramie under tension could be treated with 30–35% caustic soda and subsequently washed without any evidence of a hydrate being formed. It may be inferred, therefore, that swelling is absolutely necessary in order for the alkali to penetrate into the cellulose lattice. Also, the degree of preswelling definitely helps to determine the amount of alkali absorbed and the crystal structure formed when cellulose is treated in an alkali solution of a given concentration.

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[42] H. Neumann, Dissertation, Dresden, 1933.

[43] W. Schramek and H. Görg, *Kolloid-Beihefte*, **42**, 302 (1935).

[43a] K. Lauer, *Makromol. Chem.*, **7**, 5 (1951).

[44] H. Sobue, *J. Soc. Chem. Ind., Japan,* **43,** B24 (1940).

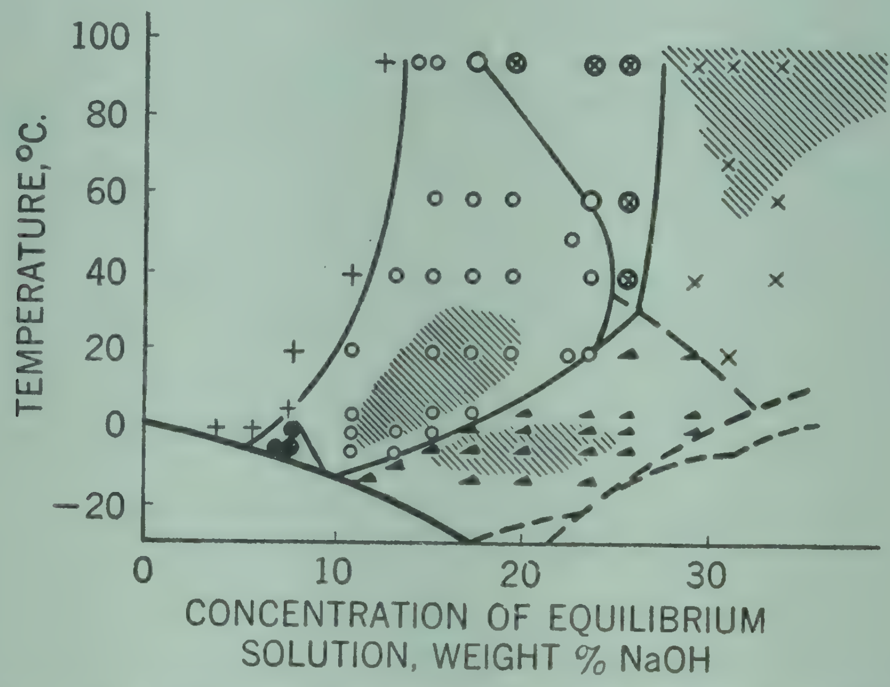

Fig. 49. Changes in the x-ray diffraction diagrams of alkali cellulose due to temperature and concentration of alkali in solution (Sobue[44]).

⊗—Alkali cellulose III
○—Alkali cellulose I
●—Alkali cellulose Q
+—Native cellulose
×—Alkali cellulose II
▼—Alkali cellulose V.

The most recent analysis of the physical changes which occur in cellulose as a result of mercerization is contained in three papers by Rånby.[45] Rånby studied the mercerization of cotton linters versus wood pulp fibers using water sorption, x-rays, and electron diffraction methods to establish the different alkali concentration ranges required to produce marked changes in water sorption and fine structure. He found that increased water sorption precedes changes detectable by x-rays or electron diffraction and that changes in wood pulps normally occur at concentrations of alkali approximately 2% lower than those producing similar changes in cotton cellulose. For native cellulose water sorption is probably a surface phenomenon since water does not enter the lattice, but with mercerized cellulose, water is absorbed both intermicellarly and intramicellarly. The conclusion is drawn that the alkali concentration necessary for transition is related to the water sorption of the original native cellulose fibers as both processes involve reaction with hydroxyl groups. Differences observed between celluloses are thus in line with the hydroxyl accessibility in the native state. Rånby also found that the micelle strings in wood cellulose are 10–20 A. thinner than those of cotton cellulose, a factor which further increases the active surface in favor of wood cellulose.

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[45] B. G. Rånby, *Acta Chem. Scand.*, **6**, 101 (1952).

Rånby also obtained data on the adiabatic mercerization of cellulose and concluded that the transformation of wet native cellulose to wet mercerized cellulose is an exothermic and natural process at room temperature and atmospheric pressure. Wet native cellulose is considered the unstable state under these conditions assuming that the cellulose fibers contain both crystalline and noncrystalline substances. The relative stability of native versus mercerized cellulose is known to be affected by temperature. Although cellulose II can readily be formed from cellulose I at ordinary temperatures, the work of Kubo[46] and Hermans[47] has shown that the reverse process can only occur at high temperatures. From these considerations, Rånby has concluded that cellulose crystals are built up in *vivo* as the chains and fibers grow, leading to lattice cellulose I, rather than synthesized as individual chains which later aggregate and crystallize in *vitro* in the presence of water. He has further suggested that both chains and crystals form under specific enzyme action.

(g) CHEMICAL REACTIONS OF ALKALI CELLULOSE

Although the consensus of opinion favors an addition compound as the most likely structure for alkali cellulose, its properties, from a purely chemical standpoint, are consistent with those of a metal alcoholate derived from a polymeric carbohydrate containing reactive hydroxyl groups. Alkali cellulose reacts with halogen compounds to form ethers:

$$R_{\text{cell}}(\text{OH})\cdot\text{NaOH} + \text{RCl} \longrightarrow R_{\text{cell}}(\text{OR}) + \text{NaCl} + \text{H}_2\text{O}$$

Alkali cellulose also reacts with acid anhydrides and acid chlorides to form esters:

$$R_{\text{cell}}(\text{OH})\cdot\text{NaOH} + \text{ROCl} \longrightarrow R_{\text{cell}}(\text{OOR}) + \text{NaCl} + \text{H}_2\text{O}$$

Undoubtedly, the most important ester prepared from alkali cellulose is sodium cellulose xanthate obtained through reaction with carbon disulfide:

$$R_{\text{cell}}(\text{OH})\cdot\text{NaOH} + \text{CS}_2 \longrightarrow R_{\text{cell}}(\text{OCSS}\cdot\text{Na}) + \text{H}_2\text{O}$$

[46] T. Kubo, *Kolloid-Z.*, **88**, 62 (1939); **93**, 338 (1940); **96**, 41 (1941).

[47] P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, pp. 155–156.

Each of these reactions is important in itself, both chemically and from the commercial point of view, but they will not be discussed in detail here as they are described thoroughly in Sections E, C, and F, respectively, of this Chapter IX.

(1) *Aging of Alkali Cellulose*

The reaction of alkali cellulose with oxygen or oxygen-producing compounds is of a somewhat different character from its other reactions in that the most important effect produced is a degradation of the cellulose brought about by combination with oxygen and subsequent splitting of the chain molecules. Cross, Bevan, and Beadle,[4] the discoverers of the viscose process, recognized that if pressed alkali cellulose is allowed to stand for any appreciable length of time, changes take place resulting in a decrease in the solution viscosity of the cellulose. This process, known as "aging," has been the subject of much study from both the practical and theoretical points of view.

Although certain early workers ascribed the effects accompanying aging solely to the action of the alkali, most of the evidence has indicated that oxygen of the air in the presence of the alkali is an essential condition of the aging process. As early as 1906, Margosches,[48] and later Ost[49] (1911), recognized oxidation as having an important part in the aging process without, however, investigating in detail the mechanism involved.

In addition to the decrease in viscosity, other major changes which cellulose undergoes during aging are an increase in the alkali solubility, a slight increase in reducing power, and the formation of carboxylic acid groups. The extent to which these changes occur depends primarily upon the oxygen concentration, the temperature, and the duration of the aging, but is also affected by the origin and previous history of the cellulose, the concentration of the steeping solution, the press ratio (weight of alkali cellulose to cellulose), and the presence or absence of certain oxidation catalysts or inhibitors.

In the past, some investigators have minimized the influence of oxygen and assumed that aging is mainly a continuation of physical changes initiated by swelling of the cellulose in a strong solution of caustic soda. It has been postulated that swelling results in a breakdown of secondary valence forces holding the micelles or cellulose chains together. However, it has been shown[50] that the changes undergone during aging are very different in character from those occurring during the swelling of mercerization. For example, during mercerization the cellulose swells and, because of the increase in internal surface thus created, becomes more reactive toward all types of chemical and physical attack, but undergoes almost no change in degree of polymerization. During aging, on the other hand, chemical activity, as measured by rate of hydrolysis or xanthate formation does not increase, although the solution viscosity is greatly affected.

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[48] B. M. Margosches, *Die Viskose*, 2d ed., Verlag der *Z. ges. Textil-Ind.* (*Klepzig's*), Leipzig, 1906.

[49] H. Ost, F. Westhoff, and L. Gessner, *Ann.*, **382**, 340 (1911).

New light on the mechanism of the aging process was obtained when Waentig[51] showed that no aging takes place if air is excluded by covering the cellulose with liquid caustic soda. After this observation, various studies were made with the object of determining more exactly the rate of oxygen absorption and the role played by oxygen in the aging process. The first investigators to measure carefully the amount of oxygen absorbed were Weltzien and zum Tobel,[52] who found that alkali cellulose prepared from an 18% solution of caustic soda reached a maximum absorption of 140 cc. of oxygen per g. of cellulose after exposure for 360 hrs. at 60°C. These investigators also found that the absorption of oxygen passes through a maximum by steeping in solutions of about 25% caustic soda. The conditions used in these experiments were, of course, extreme but indicate clearly that cellulose can be oxidized to a considerable extent.

Among the products of oxidation found by Weltzien and zum Tobel were several acidic compounds including considerable amounts of carbon dioxide. These products neutralized much of the alkali originally present and caused the oxygen consumption to slow down toward the end of the experiment. This indicated that the concentration of alkali present is also of importance in the aging process. The same investigators studied the aging of alkali cellulose in an atmosphere of nitrogen or hydrogen, or covered with an organic liquid which prevented contact with the atmosphere. Under these conditions, oxidation was greatly retarded but aging was not eliminated completely. Banderet and Rånby[53] have used this type of experiment as a means of studying cellulose structure. They observed a small but definite decrease in the molecular weight of cellulose treated with alkali in the absence of oxygen and concluded that the glucose residues of the cellulosic chain are joined principally by β-glucosidic bonds, but that cellulose must also contain another type of bond, possibly ester groups which are readily broken by alkali alone.

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[50] O. Faust and P. Karrer, *Helv. Chim. Acta*, **12**, 414 (1929); S. M. Lipatov and N. A. Krotova, *Iskusstvennoe Volokno*, **7**, 1112 (1930); S. M. Lipatov and E. Ya. Vinetskaya, *Iskusstvennoe Volokno*, **5**, 2; **6**, 2 (1931); Z. A. Rogovin and M. Schlachover, *Iskusstvennoe Volokno*, **5**, 3 (1933).

[51] P. Waentig, *Kolloid-Z.*, **41**, 152 (1927).

[52] W. Weltzien and G. zum Tobel, *Ber.*, **60B**, 2024 (1927).

[53] A. Banderet and B. Rånby, *Helv. Chim. Acta*, **30**, 1190 (1947).

Staudinger and Jurisch[54] showed that in a high vacuum practically no aging of alkali cellulose occurred even after standing for 8 days at 20°C. and that aging was very slight after a similar treatment at 100°C. Staudinger followed the changes occurring during aging by measuring the viscosity of cellulose solutions in low-concentration cuprammonium hydroxide solvent. The conclusion was drawn that the changes in alkali cellulose produced by aging are due entirely to degradation of the cellulose molecule by atmospheric oxygen. It was also shown that the oxygen consumed during normal aging increases with the amount present, but aging will proceed with very small concentrations. For a given concentration, the amount of oxygen consumed is linear with time and is quite small for ordinary alkali cellulose. The curve for aging time versus viscosity is a hyperbola, and the logarithm of the viscosity forms a straight line when plotted against the logarithm of the time.[55]

The mechanism of the degradation of alkali cellulose by oxygen is so complex that early explanations were necessarily incomplete or erroneous. Now that the course of so many oxidations has been clarified in terms of a free-radical mechanism, it appears logical to apply the same concepts to alkali cellulose. A very promising start in this direction has been made by Entwistle, Cole, and Wooding.[56] They have found that the initial course of the reaction is governed by the nature of the easily oxidizable end-groups and impurities that may be present. After the initial period, all types of cellulose tend toward the same rate of degradation. Both the initial and the later stages of the oxidation can be influenced by the usual oxidation catalysts and inhibitors. Of course, the strongly alkaline nature of the medium has to be kept in mind when parallels with other oxidations are drawn. (The kinetics of the aging of alkali cellulose are discussed in more detail in Chapter III-C-1.)

(a) Practical Applications of the Aging Reaction. From the technical standpoint, it is more important to appreciate the influences of certain chemical and physical factors affecting the aging process than to understand fully the chemical mechanism of the process. Aging is principally of interest as a method of controlling solution viscosity, and changes in viscosity are the criteria for estimating the degree of aging produced. The degree of aging may be determined conveniently by a cuprammonium or cupriethylenediamine viscosity measurement of the regenerated celluloses or by xanthation of the aged alkali cellulose and measurement of the viscosity of the resulting viscose. The effect of time on aging and viscosity has already been mentioned and may conveniently be followed by means of a log-log curve. Temperature, as might be expected, has a marked effect on aging, and the rate of change in viscosity at 65°C., for example, is approximately twenty times that at 25°C. (Fig. 50).

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[54] H. Staudinger and I. Jurisch, *Zellstoff u. Papier*, **18**, 690 (1938).

[55] O. Eisenhut, *J. prakt. Chem.*, **157**, 338 (1941).

[56] D. Entwistle, E. H. Cole, and N. S. Wooding, *Textile Research J.*, **19**, 527, 609 (1949).

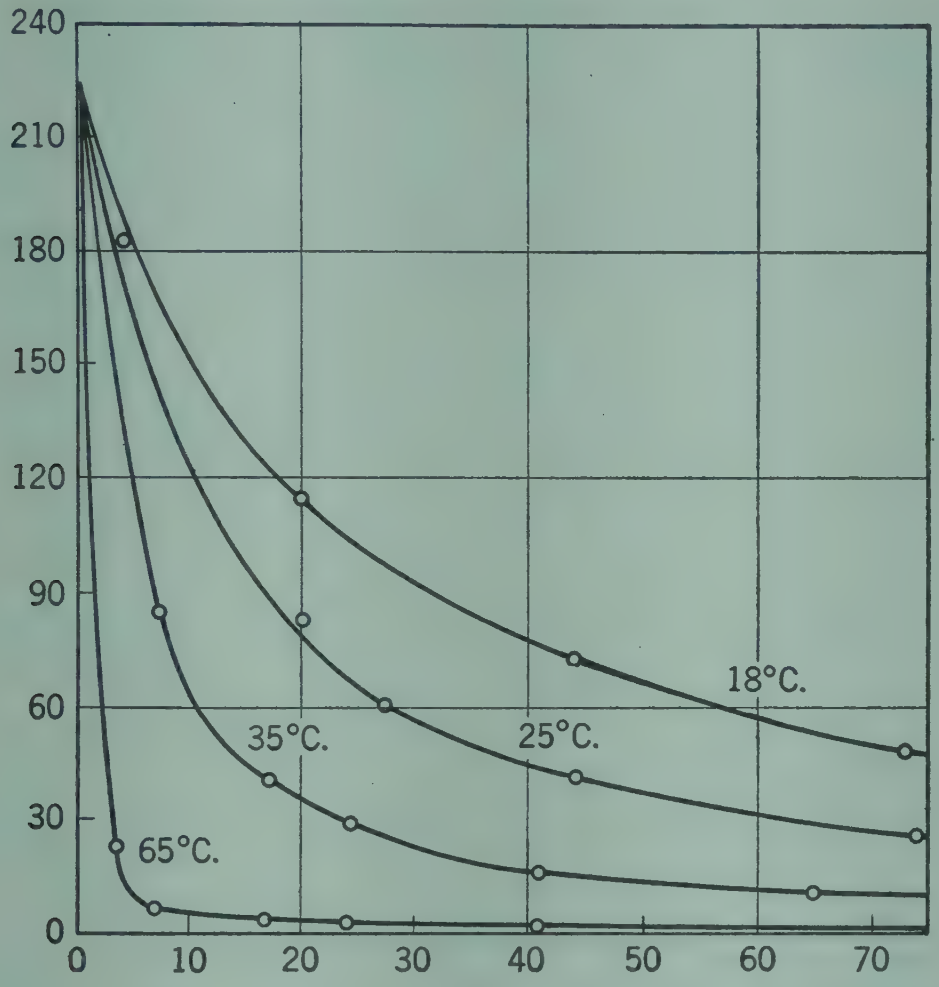

Fig. 50. Effect of temperature on rate of aging of alkali cellulose (courtesy of Conaway).

Ordinate: Cuprammonium viscosity in centipoises.
Abscissa: Aging time in hours.

The type of cellulose affects the rate of aging. It appears probable that the major reason is that differences in swelling characteristics of the different types of cellulose affect the amount of surface available for reaction with oxygen. The presence in cellulose of certain metallic impurities is also known to be important because they can act as catalysts for the oxidation reaction. In any case, it is usually necessary in the viscose process to determine the rate of aging for each new type of cellulose used. Recently Mitchell[57] has shown by use of an accelerated aging test (2 hrs. at 50°C. in

[57] R. L. Mitchell, *Ind. Eng. Chem.*, **43**, 1786 (1951).

oxygen) that differences in aging requirement of different pulps may be expressed in terms of two factors, the initial degree of polymerization and the degradation rate. Figure 51 illustrates this in the form of straight-line relationships on a semilogarithmic plot.

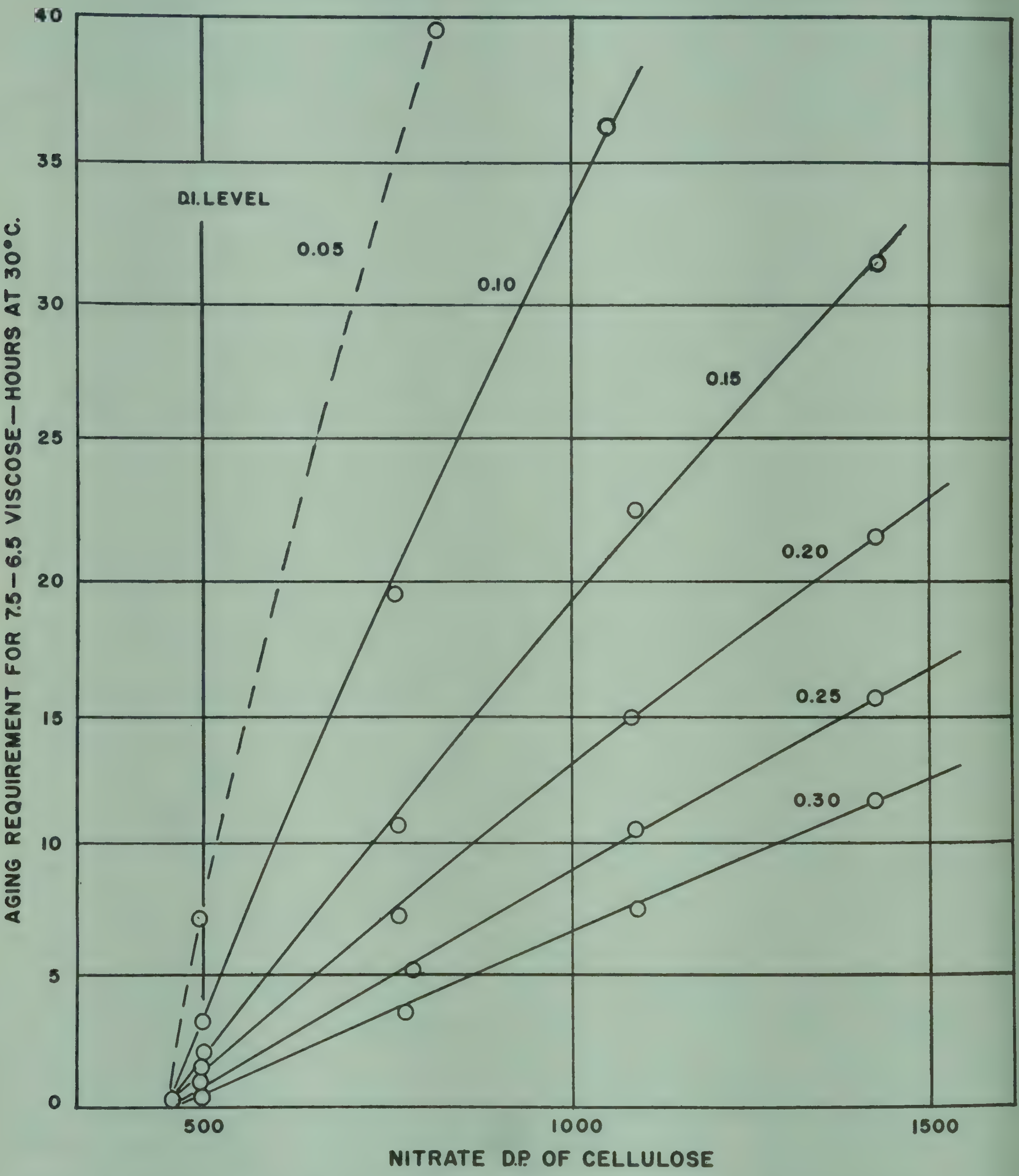

Fig. 51. Relationship of degree of polymerization (D.P.) to aging requirement at various degradation increase (D.I.) levels by accelerated test (Mitchell[57]). Degradation increase occurs when the alkali cellulose prepared by steeping in 18% NaOH is aged 2 hrs. at 50°C. in oxygen.

The concentration of alkali in the steeping liquor also affects aging, which, as has been shown, increases with increase in the concentration of caustic soda up to about 25% NaOH. However, under commercial conditions in the viscose process, this variable is not generally encountered, since the solution used almost always contains between 17 and 18% NaOH. As the press ratio is decreased, the time required to reach a given viscosity increases. It is not known whether this effect is due to the decrease in the total alkali contained in the pressed alkali cellulose, or to the fact that the alkali cellulose is generally shredded less efficiently at low press ratios.

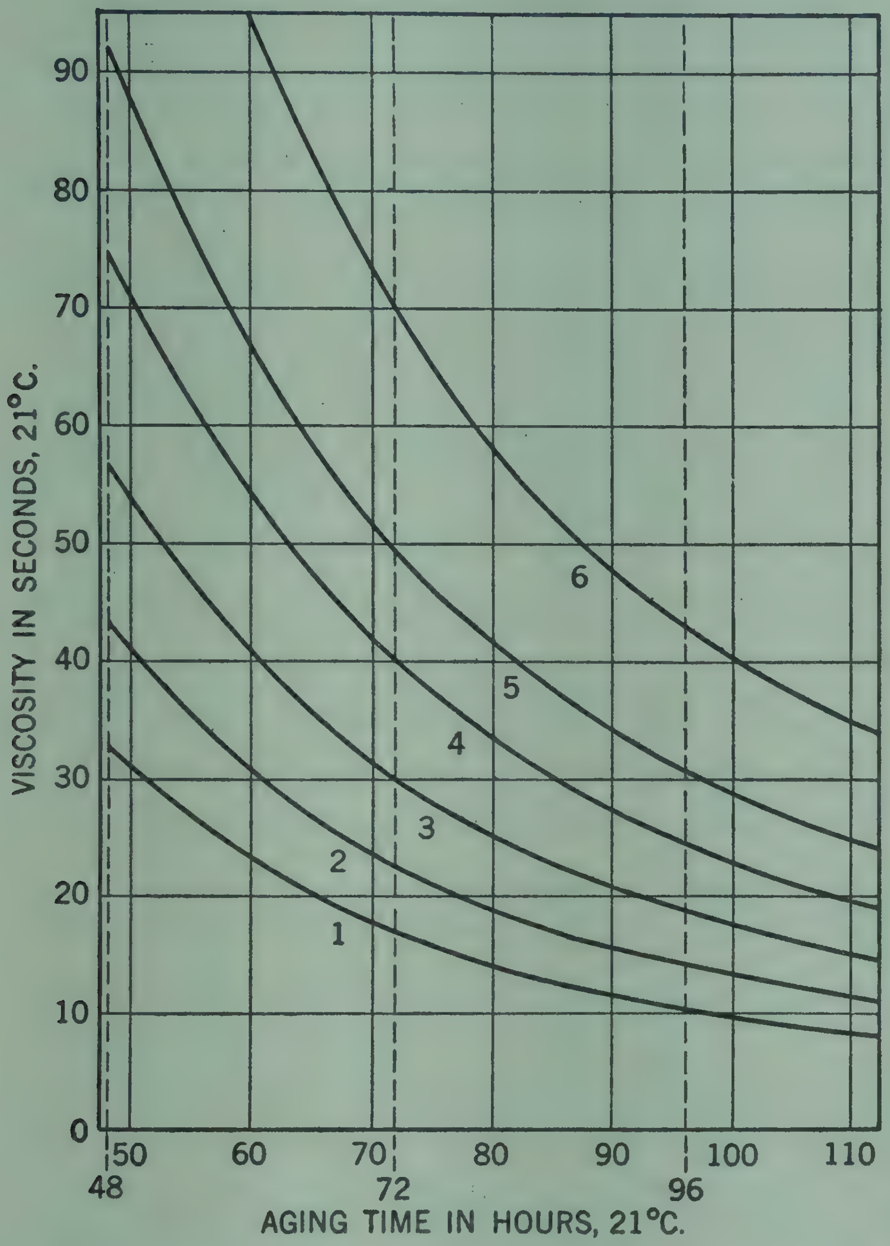

Fig. 52. Effect of iron in steeping caustic on rate of aging of alkali cellulose (Hooker, Ritter, and MacLaren[58]).

Curve	1	2	3	4	5	6
Parts Fe per million parts NaOH	128	64	32	16	9.6	4

Before this discussion of aging is concluded, mention should be made of the effects produced by certain metal ions which may be present, either in the pulp or in the steeping caustic, and which exert a catalytic effect on the oxidation process. Iron has long been recognized as a factor affecting the rate of aging, and Hooker and his coworkers[58] give data on the quantitative relation between iron content in the steeping caustic and the rate of viscosity reduction during aging (Fig. 52). The effect of manganese is almost ten times that of iron,[59] and nickel has also been shown to catalyze aging; copper inhibits the reaction slightly. Cowling[60] found that manganese apparently increases the efficiency of the oxidation reaction and produces a greater loss in viscosity for a given amount of oxygen than can be obtained without manganese present. Other substances known to accelerate the rate of aging are sodium sulfide and certain materials of organic origin such as polyhydric alcohols. Phenolic-type compounds, on the other hand, act as antioxidants and are known to retard the aging process. Finally, various active oxidizing agents such as peroxides and hypochlorites may be added to the steeping caustic to accelerate the aging process.

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[58] A. H. Hooker, B. H. Ritter, and S. F. N. MacLaren (to Hooker Electrochemical Co.), U. S. Patent 2,079,120 (May 4, 1937); *Chem. Abstracts*, **31**, 4495 (1937).

(2) *Industrial Preparation of Alkali Cellulose*

Production of alkali cellulose in the viscose rayon industry is normally accomplished by steeping the cellulose in the form of sheets set on edge in a large horizontal tank equipped with a powerful hydraulic ram movable lengthwise through the tank. Both the steeping and pressing out of the excess caustic soda solution are accomplished in the one piece of equipment. The time of steeping normally is from 30 min. to 1 hr., after which the excess liquor is drained off, the ram is started, and the sheets of alkali cellulose are pressed to the desired degree, usually to about three times the original weight of the cellulose.

After the alkali cellulose is formed, the next step in the process is to shred or disintegrate the pressed sheets so as to produce a material having the large surface essential for uniform reaction with carbon disulfide. Shredding is normally done in large disintegrators of the so-called Werner-Pfleiderer type equipped with heavy rotating arms operating against a serrated saddle. The shredders are jacketed for circulation of hot or cold water in order to control temperature, because aging is already under way at this stage as a result of removal of the excess caustic liquor by pressing. After the shredding operation, the aging process proper is completed by storing the alkali cellulose crumbs in metal or fiber containers under conditions of constant temperature. For a fuller discussion of this process, see Section F of this Chapter IX.

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[59] F. E. Bartell and H. Cowling, *Ind. Eng. Chem.*, **34**, 607 (1942).

[60] H. Cowling, Dissertation, Michigan, 1939.

Except for a general increase in the size of the equipment units used in the foregoing operations, few fundamental changes have been introduced in the methods of making alkali cellulose since the early days of the industry. Proposals have been made[61] to modify the process to make it conform more nearly to modern continuous methods of manufacture, but progress in this direction is slow. One such method[62] starts with the pulp in the form of large rolls in place of sheets, and the continuous web of cellulose is led through a long steeping tank at the end of which the excess liquor is squeezed out between closely set rolls having a uniform clearance. The pressed alkali cellulose is then immediately passed in festoons through a large enclosed chamber where the aging is accomplished quickly at a somewhat higher temperature than that used in the standard process. In the final step of the process, the web of alkali cellulose is broken up by putting it through a shredding machine consisting essentially of a barbed roller which tears the pulp apart uniformly. An alternative procedure is to shred the alkali cellulose before aging and to accomplish aging either by passing the shredded material in the form of a loose blanket through an oven, or by passing it slowly through a cylinder of large diameter which rotates on a fixed axis somewhat after the manner of a cement kiln. Alkali cellulose can also be produced by a slurry steeping process with either water-wet pulp taken directly from the pulp mill or dried sheets which are beaten up in a tank with a mercerizing solution of caustic soda. This method offers the possible advantage that it insures a uniform reaction between the cellulose and caustic soda. Removal of the excess alkali may be accomplished conveniently by centrifuging, by passing the material through spaced rollers, or by formation of a web such as can be done on a paper machine. The pressed alkali cellulose may then be disintegrated by any of the methods discussed above.

2. Mercerization of Cellulosic Textiles[63]

Mercerization, the term applied to the treatment of cotton yarns and fabrics with concentrated aqueous alkali, is carried out by the textile industry to effect desirable improvements in luster, dye affinity, and strength.

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[61] A. Faberj, *Seta Artificiale,* **4,** 3 (1932); O. Faust, *Z. Ver. deut. Ing.,* **80,** 981 (1936).

[62] F. Steimmig, German Patent 604,015 (Oct. 17, 1934); *Chem. Abstracts,* **29,** 926 (1935).

[63] This section is in part a revision of pertinent material in that on "Mercerization" prepared by E. I. Valko for the first edition.

In addition, secondary changes in "handle," uniformity, elasticity, and chemical reactivity of material may often be important. Although several of these properties may be of interest to the mercerizer, it is not possible to obtain the maximum degree of improvement in all properties simultaneously. The greatest luster is obtained by mercerizing with cotton under maximum tension, but this condition reduces the improvement which can be expected in dye affinity and elasticity of the material.[64]

Mercerization continues to be an important commercial process, even after many decades of operation. During this period several hundred investigations have been carried out to elucidate the mechanism of the mercerization process. This work has enriched the knowledge of fiber structure but has not greatly influenced industrial practice. The literature on mercerization has been reviewed by Clibbens,[1] Valko,[65] and Marsh,[66] and a bibliography has been compiled by Edelstein and Cady.[67]

(a) EFFECT OF MERCERIZATION ON COTTON FIBERS

Studies of mercerization processes in connection with (a) the mechanism of the chemical interaction of cellulose and alkalies, and (b) changes of the fiber during the treatment with caustic and during subsequent washing, are discussed earlier in this section and in Chapter IV-B. Other aspects of the mercerization process and permanent changes in the properties of the fiber produced thereby will be given here.

(*1*) *Dimensional Changes of Fibers in Alkali*

When cotton fibers are treated with alkali, lateral swelling and longitudinal shrinkage occur. Both of these effects pass through a maximum when plotted against alkali concentration, and, if sodium hydroxide is the alkali, the maxima are at approximately the same concentration. For other alkalies, no general correlation between diameter and length changes of the fiber has been established.[68] The concentration of sodium hydroxide necessary to obtain a given degree of swelling depends on the external surface of the fiber. Calvert[69] has shown that "scoured" cotton (pretreated with hot dilute alkali) swells more than raw cotton whereas "rubbed" fibers having

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[64] S. M. Edelstein, *Am. Dyestuff Reptr.*, **25**, 724 (1936).

[65] E. I. Valko, *Kolloidchemische Grundlagen der Textilveredlung*, J. Springer, Berlin, 1937.

[66] J. T. Marsh, *Mercerizing*, Chapman & Hall, London, 1941.

[67] S. M. Edelstein and W. H. Cady, *Am. Dyestuff Reptr.*, **26**, 447 (1937).

[68] G. E. Collins, *J. Textile Inst.*, **16**, T123 (1925).

[69] M. A. Calvert, *J. Textile Inst.*, **21**, T293 (1930).

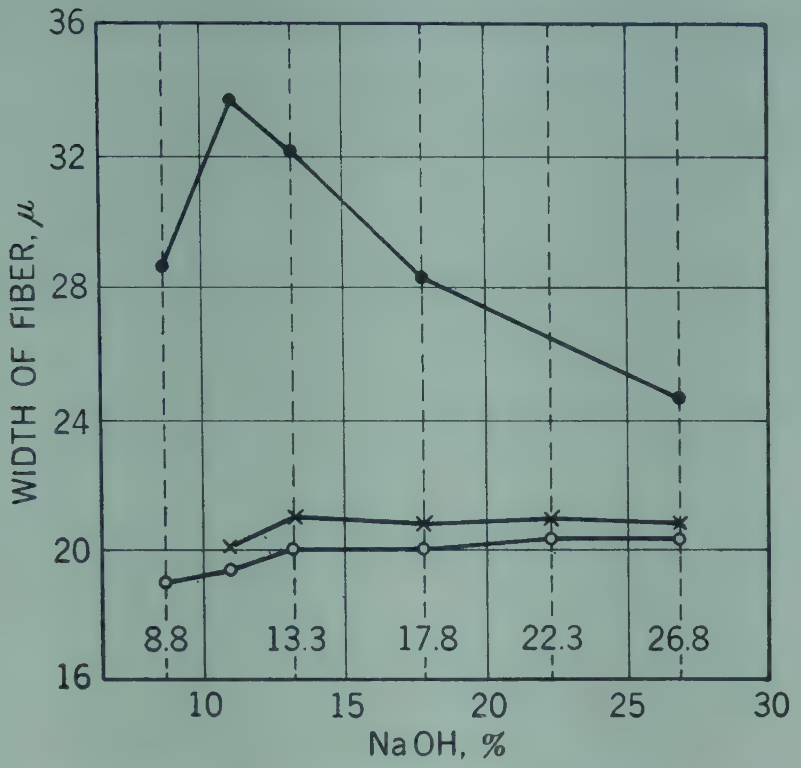

Fig. 53. Increase of the width of cotton fibers in NaOH solutions (Calvert[69]). Lower curve, raw hairs; middle curve, scoured hairs; upper curve, rubbed hairs.

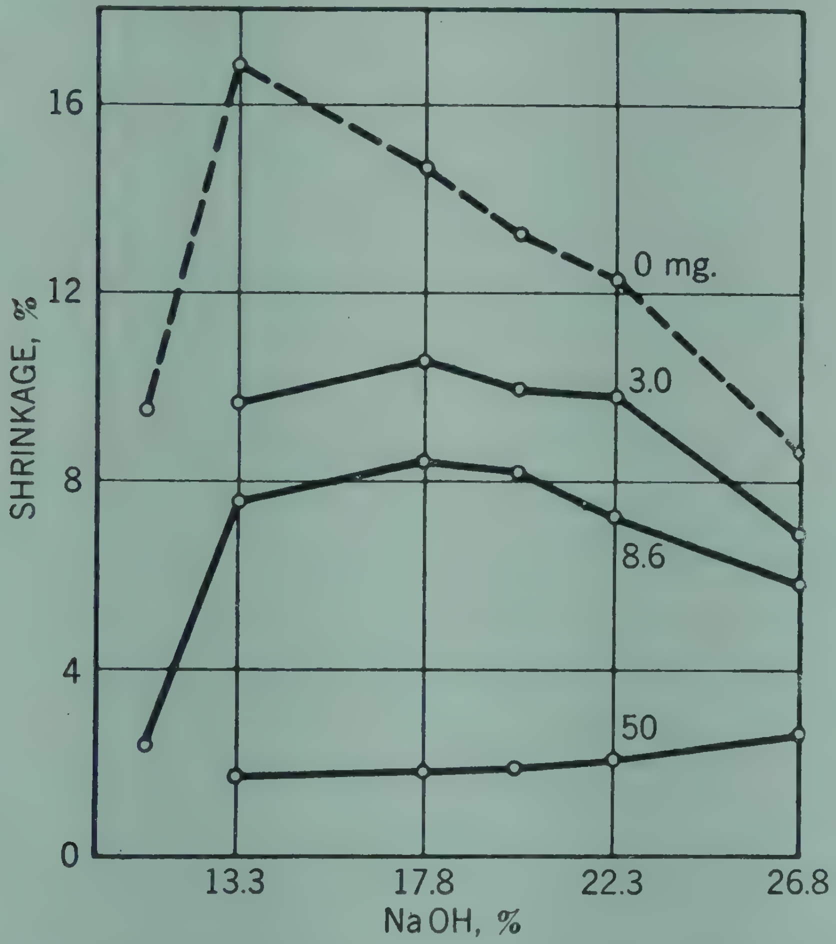

Fig. 54. Longitudinal shrinkage of scoured cotton fibers when treated under various tensions with NaOH solutions (Calvert[69]).

he cuticle (exterior surface) partially removed by an abrasive, swell even nore (Fig. 53). Corresponding effects of alkali concentration on length vere also obtained by these modifications of the fiber.[69] Usually, however, in the commercial process cellulose yarns and fabrics are treated under tension so that longitudinal shrinkage of the fiber is greatly restricted (Fig. 54).

(2) *Molecular Changes and Crystal Structure*

X-ray examination of native and mercerized cotton fibers indicates that mercerization changes the form of the crystallites (discussed in detail under "Examination of Alkali Cellulose by X-Rays" above and in Chapter IV) and increases the amount of amorphous cellulose at the expense of the crystalline material. Hermans and Weidinger[70] have developed a method for the quantitative evaluation of the crystalline fraction in cellulose fibers from intensity measurements on x-ray diffraction patterns. They have shown that mercerized cellulose has considerably less crystalline material than native cellulose. The effect of mercerization on degree of crystallinity can also be demonstrated by chemical degradative methods.[71] The degree of orientation characteristic of the crystallites in native cellulose can be either retained by application of tension as is usually done in commercial practice or increased by stretching the fibers. Without tension, orientation of the cellulose crystallites decreases.[72]

It is thought that most of the technically important changes in fiber properties occurring during mercerization do not depend on basic differences in the lattice structure between native and mercerized cellulose. Rather, they can be traced to the changes in the amount of crystalline material and to changes in the orientation of the crystallites.

Degradation of the cellulose molecule occurs in strong alkali under certain conditions. It has been demonstrated,[73] however, that fiber properties dependent on the state of polymerization remain essentially unchanged by mercerization. Staudinger[74] found that the degree of polymerization does change from 3000 to 2000 during mercerization, but this amount is inappreciable when considered in connection with mechanical properties of fibers.

(3) *Changes in Tenacity and Extensibility*

Native cellulose fibers such as cotton, flax, and ramie have high break strength and low extensibility, properties which are associated with high orientation and high crystallinity. Mercerization can cause large changes in these properties. Mercerization under tension causes an increase in tensile strength of cellulose yarns and fabrics as Langer[75] found when he mercerized scoured cotton yarn and increased its break strength 34.8%. Midgley[76] obtained data which suggest that the increase in strength of mercerized yarn is due to strengthening of individual cotton fibers and to increased cohesion between fibers. Also Edelstein[64] showed that variation of tension above that required to prevent shrinkage caused no further significant increase in break strength.

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[70] P. H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4,** 135 (1949).

[71] R. F. Nickerson, *Ind. Eng. Chem.*, **34,** 85, 1149, 1480 (1942); **39,** 1507 (1947); G. Goldfinger, H. Mark, and S. Siggia, *Ind. Eng. Chem.*, **35,** 1083 (1943); M. L. Nelson and C. M. Conrad, *Textile Research J.*, **18,** 140 (1948).

[72] G. L. Clark, *Ind. Eng. Chem.*, **22,** 474 (1930).

[73] B. P. Ridge, H. L. Parsons, and M. Corner, *J. Textile Inst.*, **22,** T117 (1931).

[74] H. Staudinger and A. W. Sohn, *J. prakt. Chem.*, **155,** 177 (1940).

The quantitative data on the effect of mercerization without tension on break strength are quite contradictory even in the case of cotton fibers which does not involve the complicating effects of yarn and fabric construction. For example, Barratt[77] found that mercerization of scoured Egyptian cotton fiber without tension lowered breaking load from 7.2 g. to 6.7 g. Greenwood[78] found no conclusive evidence that fibers from mercerized yarns lost strength. On the other hand, Clegg[79] found increases in breaking strength of 11.8% to 49.2%.

The effect of tension during mercerization on the extensibility of cellulose yarns and fibers is quite marked. Barratt[77] showed that extensibility of cotton fibers mercerized without tension increased from 7.4% to 12.2%. In the case of cotton yarn Edelstein[64] found that increasing tension from the minimum value preventing shrinkage to the maximum tension which could be applied without causing breakage reduced extensibility from 5.2% to 3.5%.

(4) *Change in Luster*

The commercial mercerizing process usually has the improvement of luster as its primary objective. The luster of cotton fabrics has been shown to be closely connected with the shape of the fiber cross section, amount of twist, alignment of the fibers in the yarn, fabric construction, and, above all, tension of the material in mercerizing solution. In caustic solution native cellulose fibers (cotton) swell immediately and their cross sections become first elliptical and then almost circular. Simultaneously, they untwist, and convolutions are eliminated. The cellulose wall swells inwardly, and the lumen almost disappears. When the caustic is washed out the cross section shrinks but retains a circular form and small lumen. These stages of swelling are shown in Figure 55.[80] Adderley[81] showed that dimensional changes of this nature have an important influence on luster. He demonstrated that the luster of cotton increases as the cross section of the fibers approaches a circular form in the case of both native and mercerized cellulose.

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[75] K. Langer, *Meilland Textilber.*, **15**, 165 (1934).

[76] E. Midgley, *Textile World*, **87**, 1382 (1937).

[77] T. Barratt, *J. Textile Inst.*, **13**, T21 (1922).

[78] R. S. Greenwood, *J. Textile Inst.*, **10**, T274 (1919).

[79] G. G. Clegg, *J. Textile Inst.*, **15**, T6 (1924).

No improvement in luster is obtained when mercerization is carried out without tension despite the fact that the resulting fibers are smoother than native cellulose and the convolutions have disappeared. The development of luster under tension is apparently due to further constriction of the lumen, formation of a more perfectly cylindrical cross section, and elimination of surface imperfections from the fibers. It is possible that removal of voids plays a part in this process. Voids (a few tenths of a micron in diameter) are thought to cause dullness in viscose rayon yarn, and, if present in or near the primary wall of cotton fibers, they would tend to collapse during swelling under tension. This would produce a more lustrous effect.

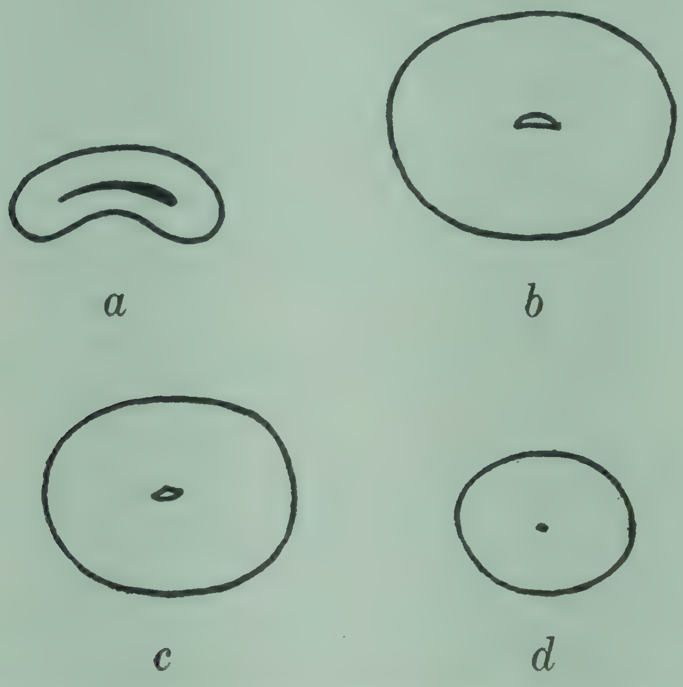

Fig. 55. Changes of the form of the cross section of cotton fibers during mercerizing (Calvert and Summers[80]). Key: (*a*) fully collapsed hair; (*b*) same, swollen in 18% NaOH solution; (*c*) same, washed with water; (*d*) same, washed and dried.

In order to explain the changes in the fiber dimensions described above, it seems necessary to assume that (a) the fiber skin exerts a mechanical restriction on the extent and direction of swelling in alkali, and (b) the arrangement of the cellulose chains, which was responsible for the collapse of the native hair, is broken up. The mechanism by which the applied tension during swelling prevents the folding of the fiber skin during subsequent drying operations is not clear.

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[80] M. A. Calvert and F. Summers, *J. Textile Inst.*, **16**, T233 (1925).

[81] A. Adderley, *J. Textile Inst.*, **15**, T195 (1924).

For materials to give the best luster after mercerization under tension, it is essential that the yarn be properly constructed. Corser and Turner[82] showed that low twist appears to be essential for maximum luster in a yarn. It is thought that double yarns, which are more lustrous than single yarns, are superior in this respect because it is possible to prepare them with lower twist and greater parallelization of the cotton fibers to the axis of the yarn.

(5) *Changes in Absorptivity and Reactivity*

Since the mercerization process decreases the amount of crystalline material and increases the separation of the cellulose chains, the resulting fibers have greater absorptive capacity and are more reactive. Moisture regain, imbibition of water, absorption of metal hydroxides or dyes from dilute solutions, as well as rates of attack by hydrolyzing and oxidizing agents, are greatly increased. These effects depend on mercerization conditions such as concentration of sodium hydroxide, tension, and temperature; consequently many tests for determining the degree of mercerization are based on absorptivity and reactivity.

Although it was long recognized that mercerized cellulose has a higher equilibrium moisture content than native fibers, Urquhart and Williams[83] for the first time made exact measurements under strictly comparable conditions with native cotton (kier-boiled) and the same mercerized without tension. They found the ratio of water contents of mercerized and native cottons to be about 1.5 which was nearly constant for all relative humidities. Figure 56 shows how this ratio depends on the tension during the mercerization and on the concentration of the sodium hydroxide solution.

Vieweg[84] observed that sodium hydroxide is absorbed from dilute alkali solution more strongly by mercerized cotton than by native. Neale[85] measured the ratio of sodium ions absorbed from 0.5% NaOH by native and mercerized celluloses in order to study the effects of specific mercerization variables. Edelstein[86] and Neale[85] also used barium hydroxide for measuring absorption ratios. The copper number of the fiber after treat-

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[82] H. K. Corser and A. J. Turner, *J. Textile Inst.*, **14**, T332 (1923).

[83] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, **16**, T155 (1925); **18**, T55 (1927).

[84] W. Vieweg, *Ber.*, **40**, 3876 (1907).

[85] S. M. Neale, *J. Textile Inst.*, **22**, T320, T349 (1931).

[86] S. M. Edelstein, *Am. Dyestuff Reptr.*, **25**, T186 (1936).

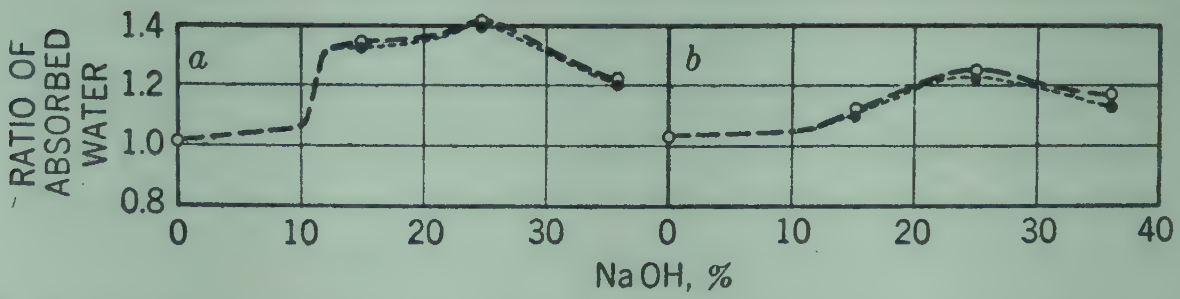

Fig. 56. Ratio of the amount of water absorbed by cotton which was treated with NaOH solutions of various concentrations, (*a*) without tension and (*b*) under tension, to the amount of water absorbed by untreated cotton (Urquhart and Williams[83]).
— — — — — — — — Adsorption - - - - - - - - - - desorption

ment with (a) 5% H_2SO_4,[87] or (b) alkali hypobromite solution[88] is greatly increased by the mercerization process and has been used to characterize reactivity of fibers.

The affinity of cotton for dyestuffs is increased by mercerization. Knecht[89] found that mercerized cotton absorbed almost twice as much dye from a given dye bath as native cotton. He also investigated the effect of tension during mercerization and drying of the fiber before dyeing and showed that these procedures reduce the effects of mercerization on the affinity for dyestuffs. Boulton and Morton[90] found that the rate of absorption of dyes is greatly increased by mercerization. Hübner[91] stated that the same shade of color is obtained if equal amounts of mercerized and native cotton are treated with the same weight of dye. Many workers in the field, however, feel that mercerized cotton requires less dye than raw cotton to produce a given shade. No quantitative tests have been reported since Hübner, and it must be assumed the apparent economy in dyestuffs is associated with the ability of mercerized cellulose to exhaust the dye bath more than native cotton. Also the increased luster would help to produce a higher brilliance of color.

(b) OPTIMUM CONDITIONS FOR MERCERIZATION

A summary of the variables which are of interest from the commercial point of view and which affect the ratio of native to mercerized cellulose in the finished product includes the previous treatment given the fibers, time and temperature of treatment, concentration of caustic, and tension on the fibers while they are in the swollen stage. Under ordinary circumstances with concentrations of 20–25% NaOH there is no advantage in the use of temperatures below 25°C.[88,92] The fibers are generally not in contact with the mercerizing solution more than one minute, and in order to get complete penetration of the fabrics or yarns in such a short time, scoured cotton is usually employed. If raw cotton is used, a wetting agent must be added to the bath. The tension applied to the material in the caustic solution is selected on the basis of the property (luster, dye affinity, strength, or extensibility) particularly desired in the finished product.

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[87] C. G. Schwalbe, *Z. angew. Chem.*, **22**, 197 (1909).

[88] C. Birtwell, D. A. Clibbens, A. Geake, and B. P. Ridge, *J. Textile Inst.*, **21**, T85, (1930).

[89] E. Knecht, *J. Soc. Dyers Colourists*, **24**, 68, 107 (1908).

[90] J. Boulton and T. H. Morton, *J. Soc. Dyers Colourists*, **56**, 145 (1940).

[91] J. Hübner, *J. Soc. Chem. Ind. (London)*, **27**, 105 (1908).

3. Metal Alcoholates of Cellulose

(a) PREPARATION AND PROPERTIES

The discovery in 1931 by Scherer and Hussey[93] of a method for preparing the trisodium alcoholate of cellulose by treating cotton linters with metallic sodium in liquid ammonia created considerable interest and speculation in cellulose chemistry, since it opened a new frontier in the investigation of the metal derivatives of cellulose. Kraus and White[94] had shown previously that when simple monohydric alcohols are treated with metallic sodium in liquid ammonia, sodium alcoholates are formed with the liberation of an atom of hydrogen for each atom of sodium consumed, according to the following reaction:

$$\mathrm{ROH} + \mathrm{Na} \longrightarrow \mathrm{RONa} + {}^{1}/_{2}\,\mathrm{H_2}$$

The formation of the alcoholates of the simple alcohols involves reaction in a homogeneous system, whereas the comparable reaction of fibrous cellulose materials with sodium in liquid ammonia involves a heterogeneous system. A quantitative study of the formation of the sodium alcoholate of cellulose by Scherer and his students showed that a mole of dry cellulose reacts with a maximum of three atoms of sodium, although any degree of substitution less than three can be obtained with the liberation of an equivalent amount of hydrogen. Schorigin and Makarowa-Zemljanskaja[95] have substantiated Scherer's results. Schmid and his coworkers,[96,97] as well as Muskat,[98] prepared the metal alcoholates of simple carbohydrates such as glucose, inulin,

[92] A. R. Urquhart, *J. Textile Inst.*, **18**, T55 (1927).

[93] P. C. Scherer, Jr., and R. E. Hussey, *J. Am. Chem. Soc.*, **53**, 2344 (1931).

[94] C. A. Kraus and G. F. White, *J. Am. Chem. Soc.*, **45**, 768 (1923).

[95] P. Schorigin and N. N. Makarowa-Zemljanskaja, *Ber.*, **69B**, 1713 (1936).

[96] L. Schmid and B. Becker, *Ber.*, **58B**, 1966 (1925).

[97] L. Schmid, A. Waschkaw, and E. Ludwig, *Monatsh.*, **49**, 107 (1928).

[98] I. E. Muskat, *J. Am. Chem. Soc.*, **56**, 693, 2449 (1934).

and water-soluble starches. According to these investigators, potassium and lithium form alcoholates with carbohydrates in the same manner as sodium, but attempts to obtain an alcoholate with calcium were not successful.

The trisodium alcoholate of cellulose is prepared by dissolving 3 moles of sodium in an excess of liquid ammonia at temperatures of −33° to −50°C. and adding 1 mole of carefully dried cellulose to the blue solution. The reaction is allowed to proceed in the absence of moisture from the air until the characteristic blue color of the solution disappears. In the absence of catalysts, this reaction requires several hours in which the rate of hydrogen evolution diminishes slowly as the reaction proceeds. The reaction rate varies with different types of cellulose and is probably determined by the accessibility of the hydroxyl groups in the amorphous and crystalline portions of the cellulose structure rather than by a specificity in the reactivity of the three hydroxyl groups in the cellulose structure. Scherer and Gotsch[99] have shown that the reaction time can be decreased from several hours to a few minutes by the addition of 1% of a sodium halide to the liquid ammonia system. The alcoholates of cellulose can probably be prepared from sodamide in liquid ammonia, since Miller and Siehrs[100] were successful in forming the potassium alcoholates of the simple carbohydrates by this method. Since sodamide is soluble in liquid ammonia to the extent of only 0.607 g. per 100 cc. at −34°C., this procedure for preparing the sodium alcoholates would probably be extremely slow.

Although attempts to prepare sodium and potassium alcoholates of cellulose by an alcohol interchange with the simple alcoholates such as sodium methylate have been unsuccessful, Harris and Purves[101] have shown that the thallium alcoholate of cellulose can be prepared by treating dry cellulose with thallous ethylate in a solution of diethyl ether or benzene. It is not possible to prepare the trithallium alcoholate of cellulose by this method, as reaction does not proceed to completion. The large thallium atoms cannot enter the crystalline portion of the cellulose structure so that only the surface hydroxyl groups are available for reaction. This steric factor enabled these workers to develop a new and ingenious method for determining the area of the internal surface or the number of available surface hydroxyl groups present in a cellulose structure by treating the thallium alcoholate of cellulose with methyl iodide and determining the extent of methylation. The internal surfaces of carefully purified ramie and of the corresponding mercerized fibers as determined by this method are 3.7×10^4 and 2.9×10^6 cm.^{2} per g., respectively.

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[99] P. C. Scherer and L. P. Gotsch, *Bull. Virginia Polytech. Inst.*, **32**, No. 11 (1939).

[100] C. O. Miller and A. E. Siehrs, *Proc. Soc. Exptl. Biol. Med.*, **29**, 535 (1931).

[101] C. A. Harris and C. B. Purves, *Paper Trade J.*, **110**, 29 (Feb. 8, 1940).

The trisodium alcoholates of chemical celluloses, such as cotton linters and wood pulp, resemble the original fibrous cellulose in physical form. These metal alcoholates are, however, unstable to moisture, oxygen, and light. When the trisodium alcoholate is exposed to atmospheric conditions, it discolors rapidly with the evolution of heat accompanied by a profound degradation of the cellulose as determined by cuprammonium viscosity measurements. Because of the high reactivity of these metal derivatives of cellulose, it is necessary to carry out reactions with these materials under carefully controlled conditions.

(b) REACTIONS OF METAL ALCOHOLATES OF CELLULOSE

In view of the chemical reactivity of the alcoholates of the simple alcohols in condensation reactions, it might be expected that the trisodium alcoholate of cellulose would be an ideal intermediate for the preparation of trisubstituted derivatives of cellulose, but this, in general, has not proved true. Miller and Siehrs[102] prepared the organic esters of cellulose by treating trisodium cellulosate with acid chlorides or anhydrides in the presence of hydrocarbon diluents. Likewise, Peterson and Barry[103] prepared various cellulose ethers by treating the metal alcoholate of cellulose with alkyl halides in the presence of hydrocarbon diluents.

Schorigin and Makarowa-Zemljanskaja[95] concluded from a study of the xanthation of the sodium alcoholate of cellulose that alkali cellulose has the structure of an alcoholate. On the other hand, Scherer and Gotsch[99] showed that the reaction of carbon disulfide with the trisodium alcoholate of cellulose is catalyzed by the presence of water and sodium nitrate. These workers report the preparation of the trisodium xanthate of cellulose by adding 2.65% of water based on the carbon disulfide to the reaction mixture which, on the basis of their reported experiments, was sufficient water to form an 11% alkali solution with the sodium present. Since the presence of limited amounts of water seems to increase the reactivity of the metal alcoholates of cellulose and since these compounds are known to be hydrolyzed readily by water, the conclusion is reached that, if alkali cellulose reacts as an alcoholate, the excess molecular sodium hydroxide present is extremely desirable and beneficial in the reaction system.

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[102] C. O. Miller and A. E. Siehrs (to North American Rayon Corp.), U. S. Patent 2,181,906 (Dec. 5, 1939); *Chem. Abstracts*, **34**, 2172 (1940).

[103] F. C. Peterson and A. J. Barry (to the Dow Chemical Co.), U. S. Patent 2,157,083 (May 2, 1939); *Chem. Abstracts*, **33**, 6595 (1939).

4. Cuprammonium–Cellulose Complexes

Schweizer[104] observed in 1857 that ammoniacal solutions of copper hydroxide dissolve certain plant and animal fibers such as cotton, linen, and silk. This important discovery is the basis of the cuprammonium or Bemberg rayon industry as well as of the viscosity determination employed in characterizing the celluloses used in the chemical and textile industries. Although many solvents for cellulose have been investigated by various workers since Schweizer's discovery, cuprammonium and cupriethylenediamine solutions are still the best solvents for all types of cellulose.

(a) PREPARATION AND PROPERTIES OF CUPRAMMONIUM SOLUTIONS

The compound formed when copper hydroxide is dissolved in aqueous ammonia solutions has the formula $Cu(NH_3)_4(OH)_2$, and the blue ammoniacal solutions of this compound are known as cuprammonium hydroxide solutions or simply as cuprammonium solutions (often abbreviated cupram). These solutions are usually prepared either by dissolving freshly precipitated cupric hydroxide in aqueous ammonia or by bubbling air over small pieces of metallic copper covered with aqueous ammonia solution. The cuprammonium solution employed by the British investigators[105] contains approximately 15 g. of copper and 240 g. of ammonia per liter, whereas the solution recommended by the American Chemical Society[106] contains 31 g. of copper and 165 g. of ammonia per liter (see Chapter XII). Many investigators add to this solution 1 to 10 g. of sucrose per liter as a stabilizing agent. In a comprehensive study, Browning, Sell, and Abel[106a] found that the copper concentration must be above 25 g./liter if all types of cellulose are to be dissolved. The ammonia concentration may vary from 125 to 250 g./liter. The viscosity of the solutions varies (in a complicated manner) with solvent composition.

Cuprammonium solution is a strong reducing agent and, in addition, is decomposed by light and by standing at room temperature for a period of several days. Due to this instability, it is necessary to use relatively fresh solutions as well as extreme precautions to protect the cellulose solutions from oxygen and as much as possible from light. The stability of cuprammonium solutions is increased by dissolved cellulose. When it is necessary to store cuprammonium for some time, it should be placed in a dark container, blanketed with nitrogen or other inert gas, and kept at a temperature of 0–5°C. Under these conditions the solution is relatively stable for several weeks.

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[104] E. Schweizer, *J. prakt. Chem.*, **72,** 109 (1857).

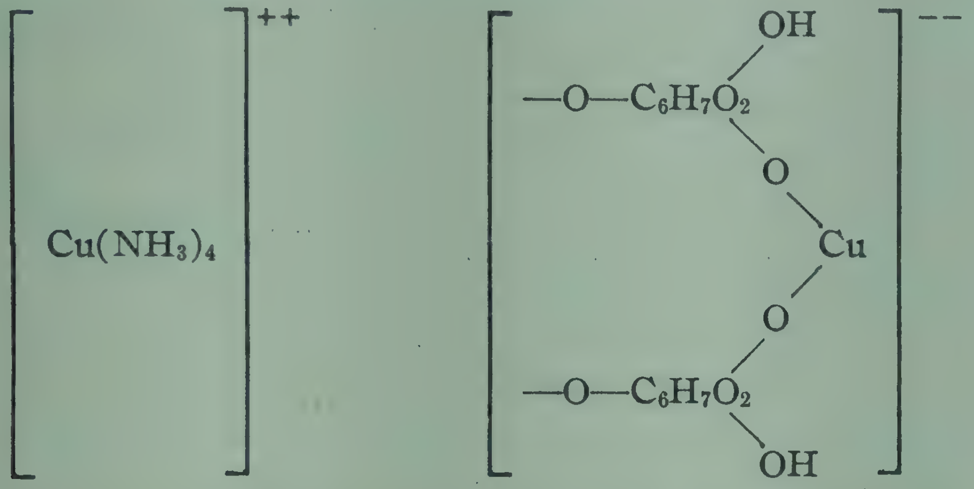
[105] *Shirley Institute Test Leaflet,* No. Chem. **7,** 1st ed., Aug., 1948; *Shirley Inst. Mem.,* **15,** 25 (1936); *J. Textile Inst.*, **27,** T285 (1936).

[106] E. K. Carver and Committee, *Ind. Eng. Chem., Anal. Ed.*, **1,** 49 (1929).

[106a] B. L. Browning, L. O. Sell, and W. Abel, *Tappi,* **37,** 273 (1954).

(b) COMPOSITION OF CUPRAMMONIUM–CELLULOSE COMPLEXES

Traube[107] was one of the first investigators to study the composition of cuprammonium–cellulose complexes. He concluded that a compound was formed in which part of the copper is bound in the cation and part in the anion. His formula can be represented as follows:



According to this formula the ratio of copper to cellulose in the complex is 1:1 although the copper is present in two different forms. Since Traube's formula conforms neither to modern knowledge of copper coordination complexes nor to the more precise information available on the copper–ethylenediamine system, it is undoubtedly incorrect.

Hess and Messmer[108] also concluded from optical rotation studies on cuprammonium–cellulose solutions that the copper is combined chemically with the cellulose but believed the compound could best be represented as a salt with the structure $(C_6H_7O_5Cu)_2 \cdot (Cu(NH_3)_4)$. Bauer[109] analyzed Hess's data from a different viewpoint and obtained typical absorption curves. He pointed out that cuprammonium solutions are colloidal and concluded that the solution of cellulose in this solvent is due only to a physical peptizing action.

Neale[110] advanced the theory that the cuprammonium–cellulose complexes are colloidal electrolytes similar to soap, in which the strong cuprammonium base forms with cellulose, which is a weak acid, a soluble basic salt of which the cation is crystalloidal and the anion is colloidal. Neale represented the reaction involved in the solution of cellulose in cuprammonium as follows:

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[107] W. Traube, *Ber.*, **54B**, 3220 (1921); **55B**, 1899 (1922); **56B**, 268 (1923).

[108] K. Hess and E. Messmer, *Kolloid-Z.*, **36**, 260 (1925).

[109] E. Bauer, *Kolloid-Z.*, **36**, 257 (1925).

[110] S. M. Neale, *J. Textile Inst.*, **16**, T363 (1925).

$$(C_6H_{10}O_5)_n + n\ Cu(NH_3)_4(OH)_2 \longrightarrow n\ [Cu(NH_3)_4]^{++} + [C_6H_9O_5^-]_n + n\ [OH]^- + n\ H_2O$$

This formula differs from Traube's in that all of the copper is bound in the cation. The ratio of copper to cellulose, however, is 1:1, and Neale confirmed this ratio by analyzing the precipitated and purified cuprammonium–cellulose complex. Lieser[111] has proposed still another formula which can be considered as a modification of Traube's and Neale's proposals in which 1.5 moles of copper are combined with each cellulose or anhydroglucose unit.

One of the most interesting investigations in this field was carried out by Jolley[112] in which cuprammonium solutions containing insufficient copper to effect complete solution of the cellulose fibers were studied. Under these conditions it was possible to determine the concentration of copper at equilibrium in both the solid and dissolved phases. With this technique it was possible to show that the equilibrium concentration of copper in the cellulose solution is appreciably lower than in the original solvent due to preferential absorption of the copper by the undissolved cellulose. Jolley also showed that the addition of small amounts of sucrose to cuprammonium solutions as a stabilizing agent decreases the solvent action of the solutions. In view of the fact that the highest concentration of copper employed in Jolley's tests was only 5 g. per liter and the dissolved phase contained 0.75 mole of copper per mole of cellulose, it is certainly reasonable that in conventional solutions which contain from 15 to 31 g. of copper per liter, the ratio of copper to cellulose in the complex would increase to unity as proposed by Traube and other investigators. Stamm[113] and Kraemer,[114] in determining the molecular weight of cellulose by the ultracentrifuge method, assumed that in the cuprammonium–cellulose complex, 1 mole of copper is combined with each mole of cellulose.

The difficulties in obtaining analytical information on the cuprammonium–cellulose complex are due to the high vapor pressure of ammonia and the great excess of ammonia that is present. According to the Traube formula, ammonia should be liberated from the copper–ammonium hydroxide compound by reaction with cellulose. Attempts by various workers such as Berl and Innes[115] to determine if the vapor pressure of the ammonia increases when cellulose is dissolved in cuprammonium solution have not been entirely successful. One method of eliminating this objection is to replace the ammonia with a higher boiling amine such as ethylenediamine. In fact a considerable portion of the structural work on cuprammonium complexes has been done with the copper hydroxide–ethylenediamine complex, which has the formula $Cu(NH_2CH_2CH_2NH_2)_2(OH)_2$ and is usually represented as $Cu(en)_2(OH)_2$. A similar complex has been reported by Jayme[115a] for cobalt and ethylenediamine. This complex was also found to be a solvent for cellulose.

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[111] T. Lieser, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 272 (1938).

[112] L. J. Jolley, *J. Textile Inst.*, **30**, T4 (1939).

[113] A. J. Stamm, *J. Am. Chem. Soc.*, **52**, 3047, 3062 (1930).

[114] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935); E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

Jolley,[116] in attempting to determine the structure of cuprammonium complexes, also worked with the analogous diamine compounds. The conditions employed were essentially the same as for cuprammonium in which the concentration of copper was too low to effect complete solution of the cellulose, so that the concentration of copper and diamine could be determined in both the solid and solution phases. Jolley confirmed the observation that the diamines are different from ammonia in that the addition of excess ammonia to cuprammonium solutions increases the solvent action of the solution, whereas the addition of excess diamine decreases the solvent action. In copper hydroxide–ethylenediamine solutions in which the concentration of diamine was varied from 6 to 210 g. per liter, the ratio of ethylenediamine to copper was not 2:1 but varied between 1:9 and 1.78:1. Jolley concluded, as had Hoffmann,[117] that both the monodiamine complex $[Cu(en)(OH)_2]$ and the di-diamine complex $[Cu(en)_2(OH)_2]$ were formed in the copper hydroxide–diamine system. Recently, the existence of both of these forms has been confirmed by Jonassen and Dexter[118] through spectrographic analysis.

Levy and Muffat[119] have pointed out that differences in cuprammonium and cupriethylenediamine solutions of cellulose may be more apparent than real. If the ratio of diamine to copper is high (approaching that in cuprammonium solvent) precipitation does not occur on further addition of diamine. Dilution with water causes precipitation of cellulose just as in the case of cuprammonium solvent. Browning and coworkers[106a] have studied the variation of solvent power and solution viscosity with solvent composition. Jolley[106] showed that, in solutions of partially dissolved cotton, the ratio of copper to diamine in the undissolved fibers was unity. As a result of a careful study of this system, Jolley proposed the following mechanism for the solution of cellulose in copper hydroxide diamine solutions:

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[115] E. Berl and A. G. Innes, *Z. angew. Chem.*, **23**, 987 (1910).

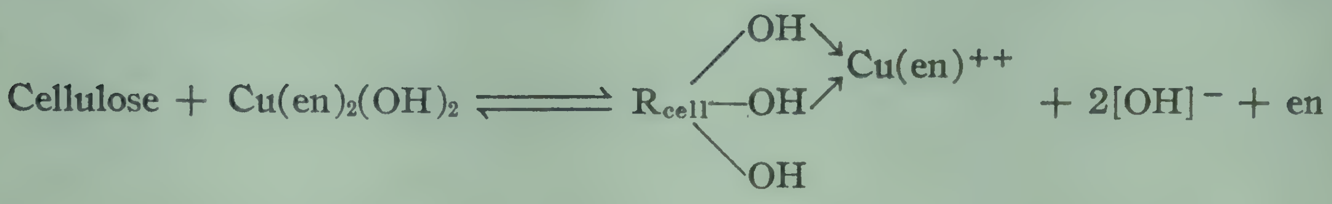
[115a] G. Jayme, *Das Papier*, **5**, 244 (1951).

[116] L. J. Jolley, *J. Textile Inst.*, **30**, T22 (1939).

[117] H. Hoffmann and N. Bruch, *Cellulosechemie*, **14**, 50 (1933).

[118] H. B. Jonassen and T. H. Dexter, *J. Am. Chem. Soc.*, **71**, 1553 (1949).

[119] R. M. Levy and P. Muffat, *Paper Trade J.*, **118**, 32 (Feb. 3, 1944).



$$\text{Cellulose} + \mathrm{Cu(en)_2(OH)_2} \rightleftharpoons \mathrm{R_{cell}}\begin{array}{l}\diagup\mathrm{OH}\searrow \\ -\mathrm{OH}\nearrow \\ \diagdown\mathrm{OH}\end{array}\mathrm{Cu(en)^{++}} + 2[\mathrm{OH}]^- + \mathrm{en}$$

In this formulation the ratio of copper to diamine in the cellulose complex is also unity.

The cuprammonium–cellulose system is complicated still further from the viewpoint of establishing a reaction mechanism by the addition of inorganic bases such as sodium, potassium, or lithium hydroxides to the solution. It was shown by the work of Traube,[107] Hess,[108] and Trogus and Sakurada[120] that the addition of small amounts (1 to 3%) of alkali hydroxides to cellulose increases its solubility in cuprammonium solutions. It is not known exactly how the sodium ions enter the cuprammonium–cellulose complex, but the most plausible mechanism is that they replace a portion of the $[\mathrm{Cu(NH_3)_4}]^{++}$ ions in the cation part of the molecule. Additional evidence for this view was obtained by Jolley,[116] who showed that cellulose reacts with copper hydroxide in the presence of sodium, lithium, and potassium hydroxides to form a cellulose–copper complex but that the complex is not soluble in aqueous solutions of these bases. Yet as pointed out by Arkhipov and Kharitonova,[121] if the cellulose–copper complex is placed in concentrated ammonia, solution takes place immediately.

However, the following tentative hypothesis may serve to rationalize the above observations. First, it is apparent that cupric ion in an alkaline medium forms a very stable complex with cellulose. This complex is insoluble and is therefore probably cross-linked, with the copper coordinated with four hydroxyls in all. These hydroxyls may be assumed to be in positions 2 and 3 of two adjoining chains. As ammonia is added, it will tend to break the cross-links by forming coordination complexes similar to Jolley's picture of cupriethylenediamine–cellulose, or a similar zwitterion-like structure formed by the ionization of the hydrogens from the two hydroxyls. A stronger complexing agent, such as ethylenediamine, can break the remaining bonds if present in excess, and thereby reduce the solubility of cellulose. Since ammonia is a weak complexing agent, it may be understood why the solubility in cuprammonium improves as the ammonia concentration is increased to the limit imposed by its solubility. In addition, it must be remembered that ammonia itself is a relatively good solvent for salt-like bodies such as the postulated complex, whereas ethylenediamine in excess will tend to precipitate the cellulose in the same manner as alcohol.

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[120] C. Trogus and I. Sakurada, *Ber.*, **63B**, 2174 (1930).

[121] M. I. Arkhipov and V. P. Kharitonova, *J. Applied Chem.* (*U. S. S. R.*), **22,** 1030 (1949); through *Chem. Abstracts*, **44,** 2233 (1950).

The reaction of cuprammonium solution with cellulose fibers is certainly heterogeneous in that the surface molecules of the structure are first attacked. The solution of the surface molecules then exposes new surfaces for further reaction. Although cuprammonium solution is unstable and is relatively difficult to prepare, it is still one of the most useful tools for characterizing cellulose.

5. Cellulose–Organic Base Complexes

The reaction of cellulose with organic bases has been primarily of academic interest. However, some of the tetraalkylammonium bases have become commercially available. Dehnert and König[122] showed that certain organic bases such as tetraalkylammonium bases, R_4NOH, and guanidinium hydroxide, $[(NH_2)_3C]OH$, are strong swelling agents for cellulose. A number of other organic bases have been investigated. Shutt[123] has shown that the trialkylsulfonium hydroxides dissolve cellulose. Hess and Trogus[124] investigated the action of certain other organic bases, such as hydrazine, ethylenediamine, and tetraethylenediamine, on cellulose and concluded from x-ray studies that these bases form definite compounds with cellulose.

Lieser and Leckzyck[125] concluded from a study of the action of tetraalkylammonium bases on celluloses that those bases having a molecular weight of approximately 150 or greater are solvents for cellulose, whereas bases of lower molecular weight are only swelling agents. They showed also that each base has a specific concentration at which it is most effective as a solvent for cellulose, and that this concentration decreases as the molecular weight of the base increases. Brownsett and Clibbens[126] con-

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[122] F. Dehnert and W. König, *Cellulosechemie,* **5,** 107 (1924); **6,** 1 (1925).

[123] R. S. Shutt (to Battelle Memorial Inst.), U. S. Patent 2,371,359 (Mar. 13, 1945); *Chem. Abstracts,* **39,** 3667 (1945).

[124] K. Hess and C. Trogus, *Z. physik. Chem.,* **B14,** 387 (1931).

[125] T. Lieser and E. Leckzyck, *Ann.,* **522,** 56 (1936).

[126] T. Brownsett and D. A. Clibbens, *J. Textile Inst.,* **32,** T32, T57 (1941).

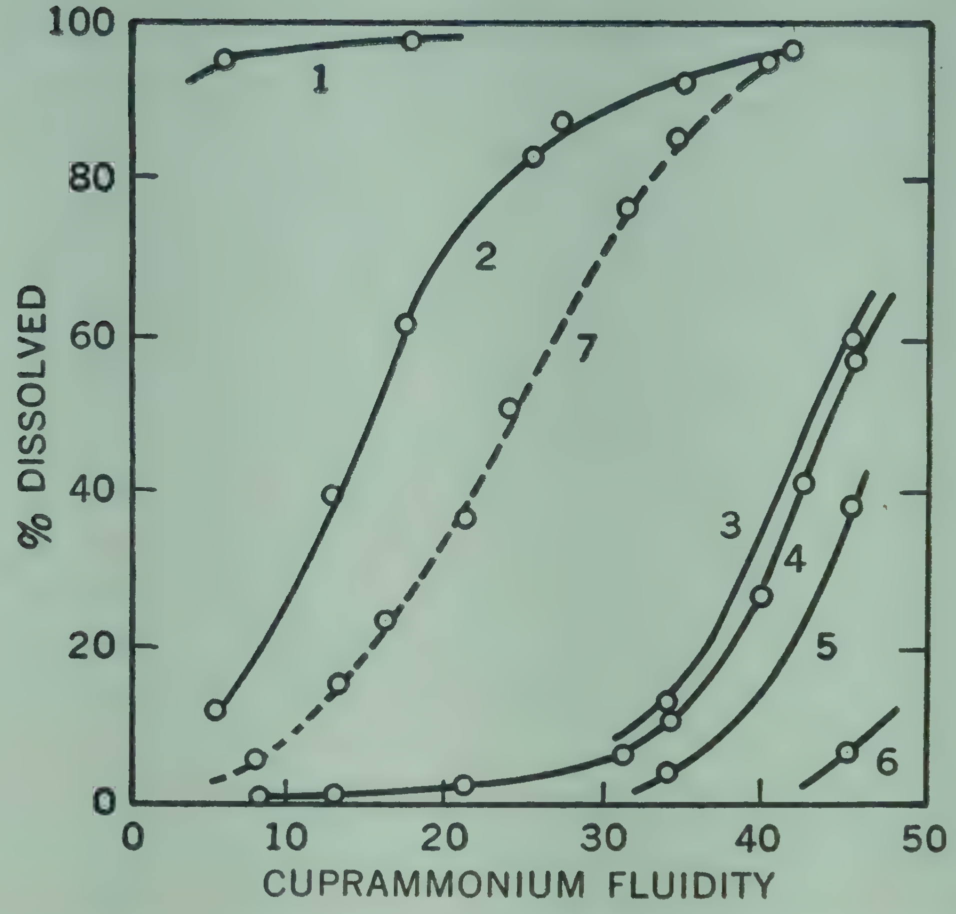

Fig. 57. Relation between fluidity of modified cottons and their fractional solubility in different bases at their optimum concentrations (Brownsett and Clibbens[126]). Curves: 1, dibenzyldimethylammonium hydroxide at 20°C.; 2, benzyltrimethylammonium hydroxide at 20°C.; 3, tetramethylammonium hydroxide at 15°C.; 4, NaOH at 15°C.; 5, LiOH at 15°C.; 6, KOH at 15°C.; 7, NaOH at −5°C.

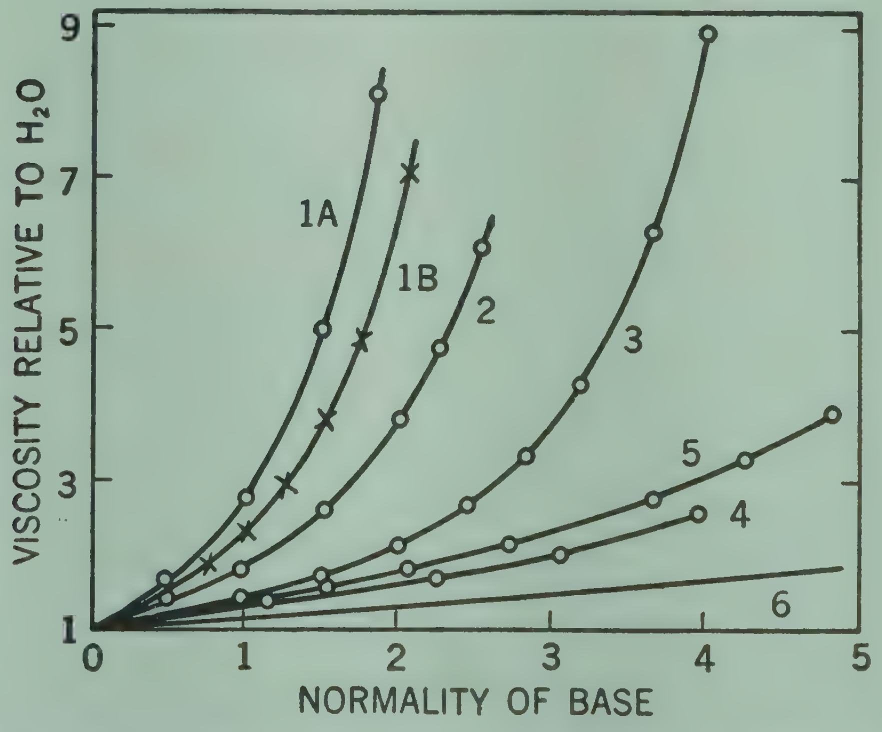

Fig. 58. Relative viscosities of aqueous solutions of different bases at 20°C. (Brownsett and Clibbens[126]). Curves: 1, dibenzyldimethylammonium hydroxide (samples A and B); 2, benzyltrimethylammonium hydroxide; 3, tetramethylammonium hydroxide; 4, NaOH; 5, LiOH; 6, KOH.

firmed the work of Lieser and Leckzyck and showed that the maximum solubility of cellulose in aqueous solutions of tetramethyl-, benzyltrimethyl-, and dibenzyldimethyl-ammonium hydroxides occurs at 2.5 *N*, 2.15 *N*, and 1.9 *N*, respectively. These workers also pointed out that there is a relationship between solvent activity and the relative viscosity of the organic bases. Thus, dibenzyldimethylammonium hydroxide, which has the greatest solvent action on cellulose, also possesses the highest relative viscosity (Figs. 57 and 58). Bases of high molecular weight, such as dibenzyldimethylammonium hydroxide, approach cuprammonium hydroxide in solvent action, since they are capable of dissolving relatively undegraded cotton linters and wood pulp fibers. Lovell[127] developed a procedure for using these solutions to determine the molecular weight of cellulose but found that it was more time consuming than the cuprammonium method. The trialkylsulfonium hydroxides described by Shutt[123] as solvents for cellulose must contain two hydrocarbon radicals of at least two carbon atoms each. The solutions have been adapted to extrusion into coagulating baths to produce shaped articles of regenerated cellulose. As in the case of the quaternary ammonium bases, the utilization of the sulfonium bases has been limited because of their high cost in comparison with inorganic bases such as sodium hydroxide.

The reactions of cellulose in aqueous solutions of the organic bases are, in general, similar to reactions in solutions of inorganic bases with the exception that in the organic bases the reactions can be carried out in homogeneous media. Lieser and Leckzyck[125] were able to prepare the trixanthate of cellulose by treating cellulose with carbon disulfide in a 3.7 *M* solution of tetraethylammonium hydroxide. Likewise, Powers and Bock[128] were able to prepare the substituted acetals and ethers of cellulose by treating cellulose dissolved in tetraalkylammonium bases with α-chloro ethers and alkyl chlorides, respectively. One possible advantage of the organic over the inorganic bases as reaction media for cellulose is that more uniform partially substituted derivatives may be obtained, since the reactions in organic bases can be carried out in a homogeneous system. Mahoney and Purves[129] have confirmed this possibility by showing that a partially ethylated cellulose prepared by a homogeneous reaction in an organic base is ethylated more uniformly than are similarly etherified celluloses prepared in the regular heterogeneous reaction from alkali cellulose.

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[127] E. L. Lovell, *Ind. Eng. Chem., Anal. Ed.*, **16**, 683 (1944).

[128] L. H. Bock and A. L. Houk (to Rohm & Haas), U. S. Patent 2,083,554 (June 15, 1937); *Chem. Abstracts*, **31**, 5577 (1937); D. H. Powers, L. H. Bock, and A. L. Houk (to Rohm & Haas), U. S. Patent 2,087,549 (July 20, 1937); *Chem. Abstracts*, **31**, 6461 (1937).

[129] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942).

E. ETHERS[1]

A. B. SAVAGE, A. E. YOUNG, AND A. T. MAASBERG

Etherification of the hydroxyls of cellulose yields technically useful products. Ethers of cellulose are organosoluble and thermoplastic, water-soluble, or aqueous alkali-soluble depending upon the kind and the degree of structural change effected.

This Section E contains, first, a review of the principles of cellulose etherification and, second, a discussion of cellulose ether manufacture in the United States. The manufacture of ethyl cellulose, methyl cellulose, carboxymethyl cellulose, hydroxyalkyl celluloses, benzyl cellulose, and cyanoethyl cellulose is discussed.

The active hydroxyls of cellulose are etherified by organic halides, alkene oxides, or olefins activated by polar substituent groups, in the presence of alkali; commonly the cellulose is treated with sodium hydroxide and the product, alkali cellulose, reacts with the etherifying reagent. Important cellulose ethers and the reagents from which they are made are:

Ether	Example	Class reagent
Alkyl	Ethyl cellulose	Alkyl halides or sulfates
Carboxyalkyl	Carboxymethyl cellulose	ω-Halocarboxylic acids or salts
Hydroxyalkyl	Hydroxyethyl cellulose	Alkene oxides or halohydrins
Aralkyl	Benzyl cellulose	Aralkyl halides
β-Substituted alkyl	Cyanoethyl cellulose	Olefins activated by polar substituent groups

1. History

Suida[2] in 1905 proposed the etherification of cellulose. He let dimethyl sulfate react with an alkali-swollen cellulose to make inactive the surface hydroxyls of the cellulose, but he did not obtain the cellulose ether as an entity. Lilienfeld[3] in 1912 and later[4] outlined the field of cellulose ether technology. He described organosoluble ethers, ethers soluble in cold but not in hot water, mixed ethers, and ethers of variant degrees of substitution (D.S.). Leuchs[5] and Dreyfus[6] in 1912 also claimed organosoluble ethers. Worden[7] described the resultant patent race.

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[1] This section is a revision of that prepared by Shailer L. Bass, A. J. Barry, and A. E. Young for the first edition of this book.

[2] W. Suida, *Monatsh.*, **26**, 413 (1905).

Denham and Woodhouse[8,9] prepared methyl cellulose as an aid to establishing the structure of cellulose (see Chapter III-B). Haworth[10] prepared methyl cellulose by the simultaneous hydrolysis and methylation of cellulose acetate. Jansen[11] described carboxymethyl cellulose in 1921; it was manufactured[12] in Germany prior to 1924. Hydroxyethyl cellulose was mentioned by Hubert[13] in 1920. Benzyl cellulose was described by Gomberg and Buchler[14]; it is manufactured in Europe, but not in the United States.

2. Chemistry of the Etherification Reaction

The etherification of cellulose usually consists of the preparation of alkali cellulose by the interaction of cellulose with a base and a solvating agent and the reaction of the alkali cellulose with the etherifying reagent. Processes in which the alkali is not consumed are: methylation of the hydroxyls of cellulose by diazomethane,[15] addition of alkene oxides, and addition of olefins activated by polar substituent groups, such as nitrile, carboxyl, or sulfonyl, to the hydroxyls of cellulose.

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[3] L. Lilienfeld, Brit. Patent 12,854 (Sept. 1, 1913); U. S. Patent 1,188,376 (June 20, 1916); *Chem. Abstracts*, **10**, 2145 (1916).

[4] L. Lilienfeld, U. S. Patent 1,683,831 (Sept. 11, 1928); *Chem. Abstracts*, **22**, 4246 (1928).

[5] O. Leuchs (to F. Bayer and Co.), German Patent 322,586 (July 1, 1920); J. K. Chowdhury, *Biochem. Z.*, **148**, 76 (1924).

[6] H. Dreyfus, French Patent 462,274 (Jan. 23, 1914); *Chem. Abstracts*, **8**, 3859 (1914).

[7] E. C. Worden, *Technology of Cellulose Ethers*, Vols. I and III, Worden Laboratory and Library, Millburn, N. J., 1933.

[8] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913).

[9] W. S. Denham and H. Woodhouse, *J. Chem. Soc.*, **105**, 2357 (1914).

[10] W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J. Chem. Soc.*, **1931**, 821.

[11] E. Jansen (to Deutsche Celluloid-Fabrik, Eilenburg), German Patent 332,203 (Jan. 22, 1921); J. K. Chowdhury, *Biochem. Z.*, **148**, 76 (1924).

[12] J. K. Chowdhury, *Biochem. Z.*, **148**, 76 (1924).

[13] E. Hubert (to F. Bayer and Co.), German Patent 363,192 (Nov. 4, 1922); *J. Soc. Chem. Ind. (London)*, **42**, 348 (1921); E. Hubert and O. Leuchs (to F. Bayer and Co.), German Patent 368,413 (Feb. 5, 1923); *Chem. Zentr.*, **1923**, 755.

[14] M. Gomberg and C. C. Buchler, *J. Am. Chem. Soc.*, **42**, 2060 (1920); **43**, 1904 (1921).

[15] R. E. Reeves and H. J. Thompson, *Contrib. Boyce Thompson Inst.*, **11**, 55 (1939).

(a) ETHERIFYING REAGENTS

The reagent used to prepare the cellulose ether influences the efficiency of the reaction. Efficiency of etherification is defined as the percentage of the reagent reacted that becomes substituent upon the cellulose. The remaining reagent consumed is converted to by-products: alcohols, glycols, ethers, or salts.

In ordinary single-phase chemical reactions, the order of reactivity of the alkyl halides decreases from iodide to bromide to chloride.

The reaction with alkali cellulose is multiphase. In the early stages the solid alkali cellulose is surrounded by a solvate that is usually aqueous sodium hydroxide; the reagent must diffuse through this solvate to the reaction centers. Methyl iodide diffuses slowly, yet it is very reactive; side reactions are more rapid than is the reaction with the cellulose. Methyl iodide is less efficient than either methyl bromide or methyl chloride. Methyl bromide is slightly less efficient than methyl chloride; the small advantage in reactivity of the bromides is offset by their greater cost.

Methyl chloride is used to manufacture methyl cellulose; ethyl chloride is used to manufacture ethyl cellulose. Alkyl sulfates are not used to manufacture these ethers in the United States. Heuser[16] has discussed the laboratory use of methyl sulfate.

The primary alkyl halides of three or more carbon atoms do not diffuse readily to the reaction zone even at high temperature (140° to 150°C.); instead, excessive by-product formation and cellulose degradation occur. If, however, the cellulose is first ethylated or methylated, it then reacts readily with the higher alkyl halides to form mixed ethers.[17-19] Thus, ease of etherification depends directly upon the rate of diffusion of the reagent to the reaction centers,[20,21] and this in turn depends upon the size of the reagent molecule. Larger molecules can enter if small molecules are used as opening wedges.

Branched-chain alkyl halides (such as isopropyl chloride) react only slightly with alkali cellulose but instead form by-products, so efficiency is poor. Schenck[22] and Timell[23] achieved etherification by using special swelling agents: Schenck alkylated sodium cupricellulose and Timell alkylated viscose rayon swelled by quaternary bases. Cellulose was methylated with diazomethane by Nierenstein[24] and by Reeves and Thompson.[15]

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[16] E. Heuser, *The Chemistry of Cellulose*, Wiley, New York, 1944.

[17] M. Hagedorn and P. Möller, *Cellulosechemie*, **12**, 29 (1931).

[18] J. F. Haskins and D. C. Ellsworth (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,102,205 (Dec. 14, 1937); *Chem. Abstracts*, **32**, 1450 (1938).

[19] The Dow Chemical Co., Midland, Mich., unpublished data.

[20] E. J. Lorand, *Ind. Eng. Chem.*, **31**, 891 (1939).

[21] K. Hess, C. Trogus, W. Eveking, and E. Garthe, *Ann.*, **506**, 260 (1933).

[22] H. Schenck, Dissertation, Berlin, 1936.

[23] T. Timell, *Studies on Cellulose Reactions*, Esselte Akt., Stockholm, 1950.

Aralkyl halides (such as benzyl chloride) are used to prepare benzyl cellulose, trityl cellulose, and similar ethers.[25] The fine structure of cellulose affects the course[26] of such reactions; this will be discussed in connection with the manufacture of benzyl cellulose.

Triphenylchloromethane (trityl chloride) was found by Helferich and Koester[27] to yield an ether (trityl cellulose) of degree of substitution (D.S.) 1.0, which was split into its components by aqueous hydrochloric acid. They concluded that only the primary hydroxyls were etherified, and this premise was later adopted by Sakurada,[28] but Hockett and Hudson[29] showed that secondary hydroxyls also react. Hearon, Hiatt, and Fordyce[30] found that 90% of the primary hydroxyls and a minor part of the secondary hydroxyls of cellulose were readily tritylated. Honeyman[31] found that the primary hydroxyls of cellulose were tritylated at 58 times the average rate of the secondary, but that the rate of the primary groups relative to the secondary rapidly decreased until all hydroxyls became equally reactive. D.S. 2 was obtained. Thus steric hindrance is a factor in etherification.

Tritylation as a research tool has been succeeded by esterification with *p*-toluenesulfonyl chloride (tosyl chloride) (see Sections A and C of this Chapter IX). The application of tosylation–iodination to cellulose ethers was reviewed by Timell.[23]

Carboxymethyl cellulose results from the treatment of cellulose with alkali and either chloroacetic acid or sodium chloroacetate. Aside from the evolution of the heat of mixing, which results in loss of degree of polymerization (D.P.) if not controlled, it matters little whether the acid, the acid salt, or the alkali is added to the cellulose first. The usual substitution is D.S. 0.8 or less, but Chowdhury[12] and McLaughlin and Herbst[32] obtained substitutions approaching 2.8 by repeated reagent additions. β-Chloropropionic acid was used to prepare carboxyethyl cellulose.[19]

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[24] M. Nierenstein, *Ber.*, **58B**, 2615 (1925); *Helv. Chim. Acta*, **92**, 150 (1914).

[25] W. Hentrich and R. Kohler (to Procter and Gamble Co.), U. S. Patent 2,284,282 (May 26, 1942); *Chem. Abstracts*, **36**, 6346 (1942).

[26] E. J. Lorand and E. A. Georgi, *J. Am. Chem. Soc.*, **59**, 1166 (1937).

[27] B. Helferich and H. Koester, *Ber.*, **57B**, 587 (1924).

[28] I. Sakurada and T. Kitabatake, *J. Soc. Chem. Ind., Japan*, **37B**, 604 (1934).

[29] R. C. Hockett and C. S. Hudson, *J. Am. Chem. Soc.*, **53**, 4456 (1931).

[30] W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *J. Am. Chem. Soc.*, **65**, 2449 (1943).

[31] J. Honeyman, *J. Chem. Soc.*, **1947**, 168.

[32] R. R. McLaughlin and J. H. E. Herbst, *Can. J. Research*, **28B**, 731 (1950).

Alkene oxides and halohydrins react with alkali cellulose to yield hydroxyalkyl celluloses. Both ethylene oxide and propylene oxide are used commercially. Morgan[33] reported water-soluble hydroxyethyl cellulose of apparent D.S. 4.1. The glucopyranose residue (i.e., anhydroglucose unit) contains but three available hydroxyl groups, so much of the apparent substitution is addition to the hydroxyls of the substituent group. Alkene oxides readily polymerize[34]; thus, ethylene oxide can react with the hydroxyls of the substituent group at least as readily as with the original cellulose hydroxyls.

Sodium β-chloroethylsulfonate reacts with alkali cellulose to yield sulfoethyl cellulose, the sulfonic acid analog of carboxyethyl cellulose. Karrer and coworkers,[35] Timell,[23,36] and others[37] have prepared sulfoethyl cellulose; its manufacture was attempted in Germany during World War II. Sodium chloromethylsulfonate does not appear to react with alkali cellulose.[19] The difference in reactivity between the methyl- and ethyl-ω-haloalkylsulfonic acids may be explained on the basis of the quanticule theory of Fajans.[38]

The addition to cellulose of olefins activated by polar substituent groups is a general method for the preparation of the sulfoethyl,[39] cyanoethyl,[40–44] carboxyethyl,[45] carbamylethyl,[46] and sulfamylethyl[47] ethers of cellulose. Etherification with acrylonitrile[40–43] yields cyanoethyl cellulose which upon complete hydrolysis yields carboxyethyl cellulose. Low temperatures and dilute alkali are necessary if the nitrile ether is to be isolated. Other attempts to introduce nitrogen onto the cellulose chain have included etherification with haloalkyl amines,[48] haloalkyl amides,[49] aminoalkene oxides,[50] and ethylenimine.[51]

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[33] P. W. Morgan, *Ind. Eng. Chem., Anal. Ed.*, **18,** 500 (1946).

[34] H. Staudinger and O. Schweitzer, *Ber.*, **62B,** 2395 (1929).

[35] P. Karrer, H. Koenig, and E. Usteri, *Helv. Chim. Acta*, **26,** 1296 (1943).

[36] T. Timell, *Svensk Papperstidn.*, **51,** 254 (1948); Swedish Patent 124,025 (Feb. 15, 1949); *Chem. Abstracts*, **43,** 9446 (1949).

[37] J. B. Dickey and J. G. McNally (to Eastman Kodak Co.), U. S. Patent 2,422,000 (June 10, 1947); *Chem. Abstracts*, **41,** 5306 (1947).

[38] K. Fajans, *Chem. Eng. News*, **27,** 900 (1949).

[39] V. R. Grassie (to Hercules Powder Co.), U. S. Patent 2,580,352 (Dec. 25, 1951); W. Neugebauer, K. Sponsel, and U. Ostwald (to Kalle & Co., Akt.-Ges.), U. S. Patent 2,132,181 (Oct. 4, 1938); *Chem. Abstracts*, **33,** 381 (1939).

[40] L. H. Bock and A. L. Houk (to Rohm & Haas), U. S. Patents 2,332,048 and 2,332,049 (Oct. 19, 1943); *Chem. Abstracts*, **38,** 1640 (1944); Brit. Patent 562,581 (July 7, 1944); *Chem. Abstracts*, **40,** 736 (1946); U. S. Patent 2,349,797 (May 30, 1944).

[41] British Thomson-Houston Co., Ltd., Brit. Patent 592,352 (Sept. 16, 1947); *Chem. Abstracts*, **42,** 2103 (1948).

[42] J. H. MacGregor (to Courtaulds, Ltd.), Brit. Patent 605,357 (July 21, 1948); *Chem. Abstracts*, **43,** 404 (1949); U. S. Patent 2,482,011 (Sept. 30, 1949); *Chem. Abstracts*, **44,** 1702 (1950); *J. Soc. Dyers Colourists*, **67,** 66, 74 (1951).

[43] J. H. MacGregor (to Courtaulds, Ltd.), Brit. Patents 636,020 (Apr. 19, 1950), 636,295 (Apr. 26, 1950); *Chem. Abstracts*, **44,** 6624 (1950).

[44] R. C. Houtz (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,375,847 (May 15 1945); *Chem. Abstracts*, **39,** 4486 (1945).

α,ω-Dihalogenated etherifying agents react at both ends with cellulose to yield insoluble, high-melting, cross-linked products[52]; such agents are more useful for the surface modification of cellulose than for the preparation of soluble or plastic products. Fluoroethylene was used to prepare ω-fluoroethyl cellulose.[53]

Unsaturated aliphatic ethers have been made with the purpose of obtaining compatibility with synthetic polymers and copolymerizability with inexpensive monomers and of preparing ethers that can be cast or formed and then rendered insoluble by baking. The ethers that have been prepared from the corresponding unsaturated halides include allyl cellulose,[19,23,54–59] crotyl cellulose,[60] and mixed ethers of these and other alkyl halides and oxides.[19] Butadiene monoxide was used to prepare 2-hydroxy-3-butenyl cellulose.[61] Charch[62] prepared a cross-vulcanized product of crotyl cellulose and butadiene, and Ushakov and Klimova[63] copolymerized allyl hydroxyethyl cellulose with sulfur dioxide. The vinylation of cellulose by acetylene[64] is claimed, but positive structural proof is lacking.

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[45] V. R. Grassie (to Hercules Powder Co.), U. S. Patent 2,539,417 (Jan. 30, 1951); *Chem. Abstracts*, **45,** 4452 (1951).

[46] L. H. Bock and A. L. Houk (to Rohm & Haas), U. S. Patent 2,338,681 (Jan. 4, 1944); *Chem. Abstracts*, **38,** 3855 (1944).

[47] V. R. Grassie (to Hercules Powder Co.), U. S. Patent 2,580,351 (Dec. 25, 1951).

[48] Kalle and Co., Akt.-Ges., German Patent 719,241 (May 20, 1938); C. L. P. Vaughan (to Hercules Powder Co.), U. S. Patent 2,591,748 (Apr. 8, 1952).

[49] J. B. Riest and W. H. Delden (to Montclair Research Corp.), U. S. Patent 2,399,603 (Apr. 30, 1946); *Chem. Abstracts*, **40,** 4229 (1946).

[50] I. G. Farbenindustrie Akt.-Ges., German Patent 726,199 (Aug. 27, 1942); *Chem. Abstracts*, **37,** 6458 (1943).

[51] H. Fink, R. Stahn, and W. K. Bitterfeld (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 2,097,120 (Oct. 26, 1938); *Chem. Abstracts*, **32,** 353 (1938).

[52] E. C. Britton and K. G. Harding (to The Dow Chemical Co.), U. S. Patent 2,216,095 (Sept. 24, 1940); *Chem. Abstracts*, **35,** 893 (1941).

[53] W. E. Hanford (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,409,274 (Oct. 15, 1946); *Chem. Abstracts*, **41,** 982 (1947).

[54] C. Dreyfus, French Patent 724,584 (Oct. 15, 1931); *Chem. Abstracts*, **26,** 4950 (1932).

[55] Gesellschaft für Chemische Industrie, Basel, Swiss Patent 144,227 (Dec. 15, 1928); *Chem. Abstracts*, **25,** 4124 (1931).

[56] Gesellschaft für Chemische Industrie, Basel, Brit. Patent 342,689 (Nov. 3, 1928); *Chem. Abstracts*, **25,** 5578 (1931).

[57] I. Sakurada, *Angew. Chem.*, **42,** 549 (1929).

[58] R. Haller and A. Heckendorn, *Helv. Chim. Acta*, **24,** 85E (1941).

[59] S. N. Danilov and O. P. Koz'mina, *J. Gen. Chem.* (*U. S. S. R.*), **18,** 1823 (1948); through *Chem. Abstracts*, **43,** 5943 (1949).

Alkylsilyl ethers have been made by reaction of cellulose with alkylhalosilanes in pyridine.[19,65,66]

(b) ALKALI CELLULOSE

Cellulose alone does not react appreciably with etherifying reagents; if the cellulose is to become reactive, it must be treated with a swelling agent and a solvating agent. The usual swelling agent is sodium hydroxide; the usual solvating agent is water. Alkali cellulose preparation consists of the treatment of cellulose with aqueous sodium hydroxide solution. (The steeping technology described in Section D of this Chapter IX is seldom used in cellulose ether manufacture.)

A concentration of 30% NaOH is generally used for the preparation of alkali-soluble ethers and of water-soluble ethers of low degree of substitution. Concentrations of from 35 to 76% are used for the preparation of ethers of higher substitution. At least two moles of sodium hydroxide per glucopyranose residue are used in the preparation of alkali cellulose for alkali-soluble ethers; three or more moles of sodium hydroxide per glucopyranose residue are used in the preparation of alkali cellulose for the higher substituted water-soluble or organosoluble ethers.

The cellulose may be bleached wood pulp or cotton linters. It must be high in alpha-cellulose content, very low in incrustants, free of metals, and uniformly absorbent of water and of sodium hydroxide solution. It must also be free of clots or knots of fibers and must not have been overdried.

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[60] F. C. Hahn (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,082,797 (June 8, 1937); *Chem. Abstracts*, **31**, 5577 (1937).

[61] D. M. Musser (to Pacific Mills), U. S. Patent 2,455,083 (Nov. 30, 1948); *Chem. Abstracts*, **43**, 1979 (1949).

[62] W. H. Charch (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,520,711 (Aug. 29, 1950); *Chem. Abstracts*, **44**, 10370 (1950).

[63] S. N. Ushakov and O. M. Klimova, *Zhur. Priklad. Khim.*, **25**, 46, 191 (1952); through *Chem. Abstracts*, **46**, 5837, 6826 (1952).

[64] A. E. Favorskiĭ, V. I. Ivanov, and Z. I. Kuznetsova, *Compt. rend. acad. sci. U. R. S. S.*, **32**, 630 (1941). V. V. Shtitevskiĭ, N. A. Oblonskaya, and N. I. Nikitin, *Zhur. Priklad. Khim.*, **24**, 1045 (1951); through *Chem. Abstracts*, **46**, 4221 (1952).

[65] H. A. Schuyten, J. W. Weaver, J. D. Reid, and J. F. Jurgens, *J. Am. Chem. Soc.*, **70**, 1919 (1948); H. A. Schuyten, J. W. Weaver, and J. D. Reid (to U. S. Secretary of Agriculture), U. S. Patent 2,562,955 (Aug. 7, 1951).

[66] M. J. Hunter (to Dow Corning Corp.), U. S. Patent 2,532,622 (Dec. 5, 1950); *Chem. Abstracts*, **45**, 1768 (1950).

Uniform penetration of the sodium hydroxide or other swelling agent throughout the cellulose is the most important factor in cellulose etherification. The swelling agent must provide alkalinity at every point in the cellulose throughout the reaction; uniform swelling of the cellulose aids the diffusion of the etherifying reagent to the reaction centers. The solvating agent (water) acts as a solvent and carrier for the sodium hydroxide, as an agent to swell and solvate the cellulose so that the etherifying reagent penetrates readily, and as a diluent for the etherifying reagent. There is almost no etherification in the absence of water.[67]

The sodium hydroxide concentration that is reached toward the end of the reaction determines the degree of substitution that is achieved.[20] When the reagent reacts with the sodium hydroxide, the final alkali concentration depends upon the initial concentration, upon the water formed, upon the sodium hydroxide added, and upon the sodium hydroxide consumed. Even in the most efficient etherification, the increase in substitution above D.S. 2.0 stops when the sodium hydroxide concentration falls to about 30%. The presence of diluents, the kind and amount of agitation, and the temperature schedule used also affect the D.S. achieved.

The etherification efficiency decreases as the water concentration increases, because hydrolysis of the reagent to by-products increases, and because the over-all driving force for the etherification of cellulose is some high power[68] of the concentration of the base used as the swelling agent.

General methods for the preparation of alkali cellulose include: (1) dipping a cellulose sheet in alkali, (2) spraying or mixing a disintegrated sheet with alkali, (3) squeezing out an alkali–cellulose slurry, and (4) adding alkali to a slurry of cellulose fibers in an inert diluent. (See Section D of this Chapter IX.)

(c) OTHER SWELLING AGENTS

The distribution of substituents in cellulose ethers made from alkali cellulose does not approach closely that calculated by statistical methods; various swelling agents other than aqueous sodium hydroxide have been proposed in order to obtain more uniform substitution. These include sodium cupricellulose (Normann compound), thallium cupricellulose, organic bases, liquid ammonia, and other inorganic bases.

[67] J. Chédin and A. Tribot, *Mém. services chim. état* (*Paris*), **33**, 168 (1947).

[68] H. M. Spurlin, *J. Am. Chem. Soc.*, **61**, 2222 (1939).

(*1*) *Sodium Cupricellulose*

Normann[69] first observed the addition compound, sodium cupricellulose, that forms when cellulose is treated with sodium hydroxide and copper hydroxide, or when alkali cellulose is treated with a copper salt. Traube[70–73] and his fellow workers methylated sodium cupricellulose. The reaction rate was more rapid and the D.S. of the product was higher than in a control experiment in which alkali cellulose was used. The solubility of the ethers from sodium cupricellulose began at very low D.S. values. Products of D.S. 0.8 were soluble in both cold and hot water. Piwonka[73] stated that the methylation took place only at the 3-hydroxyl of the cellulose, but Heddle and Percival[74] found that the 2-hydroxyl reacted also.

TABLE 15

Substituent Distribution in Methyl Cellulose from Sodium Cupricellulose (Timell[23])

	Degree of Substitution						
	0.33		0.98		1.09		1.39
Substitution	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Hydroxyl	0.20	0.18	0.41	0.45	0.40	0.45	0.40
3-Hydroxyl	0.13	0.11	0.07	0.11	0.07	0.10	0.07
6-Hydroxyl	—	—	—	—	—	—	0.10
2- and 3-Hydroxyls	—	0.02	0.25	0.21	0.31	0.27	0.34
2-, 3-, and 6-Hydroxyls	—	—	—	—	—	—	0.05

Traube's products, which were of D.S. 1.0 or less, lacked trisubstituted units; in this respect they differed from commercial methyl cellulose. It appeared that the 6-hydroxyl of the cellulose did not react; this has been confirmed by Timell.[23] Traube attributed the good solubility at low D.S. to lack of trisubstitution and to uniform distribution of the substituents along the cellulose molecules. Timell found that the substituent groups in ethers from sodium cupricellulose were distributed along the cellulose molecules in accordance with the laws of probability. This implies that all of the cellulose was equally available for etherification. Table 15 shows that typical analyses of methyl cellulose made from sodium cupricellulose agree well with values calculated from rate constants by Timell.[23] The 6-hydroxyl of the cellulose did not begin to react with the methylating reagent until the substitution exceeded D.S. 1.1. Meanwhile the entering methyl groups were forced to distribute themselves evenly in proportion to the rate constants because there was a choice between but two positions, rather than among three.

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[69] W. Normann, *Chem.-Ztg.*, **30**, 584 (1906).

[70] W. Traube and A. Funk, *Ber.*, **69B**, 1476 (1936).

[71] W. Traube, R. Piwonka, and A. Funk, *Ber.*, **69B**, 1483 (1936).

[72] W. Traube (to "Achetem"), U. S. Patent 2,140,568 (Dec. 20, 1938); *Chem. Abstracts*, **33**, 2709 (1939).

[73] R. Piwonka, *Ber.*, **69B**, 1965 (1936).

[74] W. J. Heddle and E. G. V. Percival, *J. Chem. Soc.*, **1938**, 1690.

(2) *Thallium Cupricellulose*

Traube and Funk[70] found that a complex was formed when cellulose was treated with thallium and copper hydroxides or with salts of these metals together with sodium hydroxide solution. The use of thallium cupricellulose was soon abandoned in favor of sodium cupricellulose.

(3) *Organic Bases*

The dispersion of cellulose in quaternary bases of high molecular weight was first proposed by Lilienfeld.[75] Lieser and coworkers[76–78] showed that the minimum normality of a quaternary base that was necessary to disperse cellulose was a straight-line function of the molecular weight of the base.

Bock[79] stated that those quaternary ammonium hydroxides which contain unsubstituted hydrocarbon groups would dissolve cellulose. Strangely enough, one of the most important factors contributing to the solvent power of these bases seemed to be their concentration in aqueous solution. A solution with a concentration of 35 to 50% was usually a good cellulose solvent almost without regard for the size of the alkyl or aryl groups. Tetramethylammonium hydroxide was not a useful solvent because of its low (20%) water solubility. The phenyl quaternary bases were unstable at room temperature. The benzylammonium hydroxides, such as trimethylbenzylammonium hydroxide, were more stable than aliphatic bases, were readily prepared, and are useful solvents.

Sisson and Saner[80] found that the x-ray pattern of swollen cellulose that had been compounded with an amount of quaternary base insufficient to cause dispersion indicated equal modification of all of the crystalline cellulose.

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[75] L. Lilienfeld, U. S. Patent 1,771,462 (July 29, 1930); *Chem. Abstracts*, **24**, 4630 (1930); Brit. Patent 217,166 (June 5, 1923); *Chem. Abstracts*, **19**, 398 (1925).

[76] T. Lieser, *Ann.*, **528**, 276 (1937).

[77] T. Lieser, R. Jaks, and E.-A. Glitscher, *Ann.*, **548**, 212 (1941).

[78] T. Lieser and E. Leckzyck, *Ann.*, **522**, 56 (1936).

[79] L. H. Bock, *Ind. Eng. Chem.*, **29**, 985 (1937).

[80] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **43**, 687 (1939).

Bock[81,82] prepared water-soluble methyl cellulose and ethyl cellulose with the aid of quaternary bases. He obtained water solubility at D.S. 0.6 to 0.7; he assumed that the substituents were more evenly distributed than in the usual products prepared from alkali cellulose. Compton[83] and Mahoney and Purves[84] found that the methoxyl groups in methyl cellulose that had been prepared in a quaternary base were distributed according to the laws of probability, just as they are in the methylation of sodium cupricellulose. Johnston[85] found that above D.S. 2.0 the methyl cellulose was precipitated from the quaternary base and was thereafter methylated in suspension.

Timell[23] prepared methyl cellulose, ethyl cellulose, and propyl cellulose in quaternary bases. He also prepared several branched-chain cellulose ethers from viscose rayon that was dissolved in such bases. He obtained water solubility of isopropyl cellulose at D.S. 0.5, but *n*-propyl cellulose prepared under similar conditions was not water-soluble. He attributed the solubility of the isopropyl cellulose to the ability of the branched chain to hold the cellulose chains apart.

Quaternary ammonium bases are the most useful of the organic bases, but others have been used for special purposes. Guanidine was reported to be a swelling agent for cellulose by Bock.[79] Pyridine was used by Van Dyke[19] and others[65,66] as a solvent and base in the preparation of mixed ethers from etherifying reagents (organosilicon compounds) that are highly sensitive to moisture. The reaction of pyridine derivatives with cellulose is important in textile finishing. (Stearamidomethyl)pyridinium

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[81] D. H. Powers and L. H. Bock (to Rohm & Haas), U. S. Patent 2,009,015 (July 23, 1935); *Chem. Abstracts*, **29**, 6080 (1935).

[82] L. H. Bock and A. L. Houk (to Rohm & Haas), U. S. Patent 2,083,554 (June 15, 1937); *Chem. Abstracts*, **31**, 5577 (1937); D. H. Powers, L. H. Bock, and A. L. Houk (to Rohm & Haas), U. S. Patent 2,087,549 (July 20, 1937); *Chem. Abstracts*, **31**, 6366 (1937); L. H. Bock and A. L. Houk (to Rohm & Haas), U. S. Patent 2,084,125 (June 15, 1937); *Chem. Abstracts*, **31**, 557 (1937); D. H. Powers, L. H. Bock, and A. L. Houk (to Rohm & Haas), U. S. Patent 2,216,045 (Sept. 24, 1940).

[83] J. Compton, *J. Am. Chem. Soc.*, **60**, 2823 (1938).

[84] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 15 (1942).

[85] G. G. Johnston, *J. Am. Chem. Soc.*, **63**, 1043 (1941).

chloride (Velan P. F. or Zelan A) reacts with cellulose, liberating pyridine and yielding cellulose stearamidomethyl ether on the fiber surface.[86,87]

(4) *Liquid Ammonia*

The swelling of cellulose by liquid ammonia was reported by Bernardy[88] in 1925. Hess,[89] Barry, Peterson, and King,[90] and Clark and Parker[91] applied x-ray studies to this swelling. Clark and Parker found that the swelling may amount to three times the original fiber diameter.

Scherer and Hussey[92,93] found that the ammonia cellulose can quantitatively exchange all of its hydroxyl hydrogens for sodium, liberating hydrogen and consuming three atoms of metallic sodium per glucopyranose residue:

$$R_{cell}(OH)_3 + 3\ Na \xrightarrow{\text{Liquid } NH_3} R_{cell}(ONa)_3 + {}^3/_2\ H_2 \qquad (1)$$

The sodium celluloses in liquid ammonia were etherified by Peterson and Barry,[94] by Schorigin and Makarowa-Semljanskaja,[95] by Scherer and Gotsch,[96] and by Freudenberg.[97] High substitution (for example, D.S. 2.85) is obtained under such conditions, but degradation of the cellulose may occur. The liquid ammonia was said to serve as the solvating agent in this case, but one cannot be sure that water was completely absent.[94,96,98]

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[86] R. J. W. Reynolds, E. E. Walker, and C. S. Woolvin (to Imperial Chemical Industries, Ltd.), Brit. Patent 466,817 (June 7, 1937); *Chem. Abstracts*, **31**, 8195 (1937); C. E. Mullin, *Chem. Inds.*, **47**, 404 (1940).

[87] H. A. Schuyten, J. W. Weaver, J. C. Frick, Jr., and J. D. Reid, *Textile Research J.*, **22**, 424 (1952).

[88] G. Bernardy, *Angew. Chem.*, **38**, 838, 1195 (1925).

[89] K. Hess and C. Trogus, *Ber.*, **68B**, 1986 (1935); K. Hess and J. Gundermann, *Ber.*, **70B**, 1788 (1937).

[90] A. J. Barry, F. C. Peterson, and A. J. King, *J. Am. Chem. Soc.*, **58**, 333 (1936).

[91] G. L. Clark and E. A. Parker, *J. Phys. Chem.*, **41**, 777 (1937).

[92] P. C. Scherer, Jr., *J. Am. Chem. Soc.*, **53**, 4009 (1931).

[93] P. C. Scherer, Jr. and R. E. Hussey, *J. Am. Chem. Soc.*, **53**, 2344 (1931).

[94] F. C. Peterson and A. J. Barry (to The Dow Chemical Co.), U. S. Patent 2,145,273 (Jan. 31, 1939); *Chem. Abstracts*, **33**, 3587 (1939); U. S. Patent 2,157,083 (May 2, 1939); *Chem. Abstracts*, **33**, 6595 (1939); U. S. Patents 2,232,926 and 2,232,927 (Feb. 25, 1941); *Chem. Abstracts*, **35**, 3814 (1941).

[95] P. Schorigin and N. N. Makarowa-Semljanskaja, *Ber.*, **69B**, 1713 (1936).

[96] P. C. Scherer and L. P. Gotsch, *Bull. Virginia Polytech. Inst.*, **32**, 11 (1939); through *Chem. Abstracts*, **34**, 259 (1940).

[97] K. Freudenberg and H. Boppel, *Ber.*, **70B**, 1542 (1937); K. Freudenberg, E. Plankenhorn, and H. Boppel, *Ber.*, **71B**, 2435 (1938).

[98] P. C. Scherer, Jr. (to North American Rayon Corp.), U. S. Patents 2,181,919 and 2,181,920 (Dec. 5, 1939); *Chem. Abstracts*, **34**, 2172 (1940).

The presence of a small amount of water could result in the formation of alkali cellulose in suspension in the ammonia.

The necessity of water as a swelling agent in the absence of liquid ammonia was shown by Peterson and Barry; ethylation of sodium cellulose with ethyl chloride yielded D.S. 2.06 in the presence of liquid ammonia, but only D.S. 0.04 when the liquid ammonia was removed. When water was added to the system, ethylation was again obtained.

(5) *Other Inorganic Bases*

The use of inorganic bases other than sodium hydroxide has been described.[99] In general, there is no advantage in cost or performance of other bases over sodium hydroxide.

(d) ACCESSIBILITY OF CELLULOSE TO REAGENTS

The alternative swelling agents that were just discussed (topic *c* above) are expensive, and they frequently yield products that are difficult to isolate or to purify. Alkali cellulose remains the starting material for etherification. One must therefore consider how best to prepare and to use alkali cellulose.

The question of how much of cellulose is readily reactive has been debated (see Chapter IV). Attempts to determine the accessibility of cellulose were summarized by Tarkow,[100] by Timell,[23] and by Heuser.[101] Hydrolysis and oxidative methods gave very low results that are not significant in the present case. The reaction of cellulose with sodium in liquid ammonia,[23] its reaction with formic acid and acetic anhydride,[100] and various physical methods (x-ray diffraction, density, calorimetry, equilibrium moisture regain, sorption isotherms, and deuterium exchange) indicate that both cotton linters and wood pulp are 35 to 50% accessible. Tarkow stated that these figures indicate the readily accessible region of cellulose, but they indicate neither crystallinity nor chemical convertibility.

Heuser[101] indicated that the submicroscopic structure of cellulose does not interfere with the specific reactivity of the cellulose hydroxyls relative to various reagents; for example, in the heterogeneous system, methyl and ethyl chlorides preferred the 2- position whereas ethyl sulfate appeared to react more readily with the 6- position.

Mass estimates of accessibility have not yet satisfactorily assigned the accessible region of cellulose either with respect to the individual fibers or with respect to the glucopyranose residue; many of the methods proposed are open to criticism of their basic simplifying assumptions. (See Chapter IV-B.)

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[99] H. Dreyfus, U. S. Patent 2,098,335 (Nov. 19, 1937); *Chem. Abstracts*, **32,** 353 (1938); U. S. Patent 2,181,264 (Nov. 28, 1939); *Chem. Abstracts*, **34,** 2172 (1940).

[100] H. Tarkow, *Tappi*, **33,** 595 (1950).

[101] E. Heuser, *Textile Research J.*, **20,** 828 (1950).

In commercial etherification, concern is not with the inaccessibility of large portions of the cellulose, but with small numbers of *rogue* or unreactive fibers, which can seriously impair the usefulness of a batch of a cellulose ether. The origin of rogue fibers is not apparent; they may be fibers of another species, or they may still retain such incrustants as rosin and lignin.

The prevailing trend in cellulose ether manufacture is toward continuous alkali cellulose manufacture. The time during which the pulp is in contact with the sodium hydroxide solution varies from a few seconds to a few minutes, so distribution of the sodium hydroxide solution must be rapid. This makes necessary a nearly perfect pulp sheet: a sheet uniformly absorbent of water and sodium hydroxide, uniformly formed, and free of knots and clots.

Accessibility is but one of the facets of the problems of uniform etherification. Others are sodium hydroxide penetration, reagent diffusion, molecular ratios of reactants, and substituent distribution (topic *e* below). Uniform penetration of the sodium hydroxide throughout the alkali cellulose is the most important single factor in cellulose etherification. At least two moles of sodium hydroxide per glucopyranose residue are used as 30% aqueous solution to make the lower substituted alkali-soluble and water-soluble ethers. Similarly, at least three moles of sodium hydroxide per glucopyranose residue are used as 35 to 76% or stronger aqueous solution to make ethers of high substitution.

Ready diffusion of the etherifying reagent to the reaction centers is the second most important factor in cellulose etherification. Elevated temperatures aid diffusion. Diluents equalize diffusion and reaction rates and reduce steric hindrance. Stepwise addition of reactants is often better than single addition. The ratios of sodium hydroxide, cellulose, and water to one another determine the substitution reached and the efficiency of etherification.

(e) RANDOMNESS OF ETHERIFICATION

The degree of substitution of a cellulose ether and the distribution of the substituent groups among the available hydroxyls of the cellulose molecule largely determine the solubility properties and the utility of the ether.

The hypothesis that the distribution of the substituents in a cellulose ether is random and can be calculated by statistical methods was proposed by Spurlin[68] (see Chapter IX-A). Distribution was calculated from the viewpoint that the ratio of the reactivities of the 2-, 3-, and 6-hydroxyls of the cellulose remains independent of the degree of substitution, however much the over-all reactivity may vary. Thus, all of the hydroxyls may have the same chance to react, and the substituents will be distributed among the available positions according to the laws of probability. Spurlin's hypothesis has been given exhaustive mathematical and experimental treatment by Timell.[23] Earlier workers contributed less complete data. Since rate constants depend upon the specific reaction involved, they are omitted from the following discussion.

Mahoney and Purves[84] investigated the substituent distribution in several undegraded methyl celluloses and ethyl celluloses. They determined the number of primary hydroxyl groups present by tosylation–iodination. Subtraction of the number of primary hydroxyl groups so determined from the total number of unsubstituted groups in the original alkyl celluloses left a quantity, H, which was equal to the average sum of the unreacted secondary hydroxyls.

When alkylation occurred with uniform average density along the cellulose chains (that is, homogeneously), the maximum frequency of completely unsubstituted glycol units ($G_{2,3}$) was calculated to be $H^2/4$. When alkylation occurred in localized regions of the cellulose chains (that is, heterogeneously), the probable frequency of glycol units was calculated to be $H/2$. The actual occurrence of glycol units was determined by sodium periodate oxidation. The results obtained by Mahoney and Purves[84] are shown in Table 16. The column (12) *Glycol count* shows that for the methyl celluloses the determined 2,3-glycol ($G_{2,3}$) was equal to the calculated $H/2$; the methylations were heterogeneous. For ethylation D the glycol determined was equal to the calculated $H^2/4$; the etherification in a quaternary base was homogeneous. Similarly, the low D.S. ethylations E and F were heterogeneous, but ethylation A to a commercial D.S. value was quite homogeneous. The uniform substitution of sample D is shown by its solubility in water at D.S. 0.58.

Honeyman[31] treated cotton cellulose with two different concentrations of sodium hydroxide: 45% and 90%. The resulting alkali celluloses were reacted with ethyl chloride in a manner similar to commercial practice. When 45% NaOH was used, the initially heterogeneous reaction became homogeneous after 3 hrs. When 90% NaOH was used, the initial reaction was very heterogeneous; after 3 hrs. the reaction followed much the same course as when the 45% NaOH was used, except that the glycol groups $G_{2,3}$ persisted at a higher degree of substitution. This means that some por-

TABLE 16

Substituent Distribution in Cellulose Ethers (Mahoney and Purves[84])

(1)	(2)	(3) D.S.	(4) X_6	(5) $X_2 + X_3$	(6) Total	(7) H	(8) P	(9) $G_{2,3}$	(10) $H^2/4$	(11) $H/2$	(12)	(13)
C	Methyl	0.59	0.21	0.33	2.41	1.67	0.74	0.83	0.70	0.84	$H/2$	Aqueous NaOH
B	Methyl	1.85	0.51	1.34	1.15	0.66	0.49	0.32	0.11	0.33	$H/2$	Water
D	Ethyl	0.58	0.29	0.29	2.42	1.71	0.71	0.75	0.73	0.86	$H^2/4$	Water
F	Ethyl	0.71	0.30	0.41	2.29	1.59	0.70	0.74	0.63	0.80	$H/2$	Aqueous NaOH
E	Ethyl	1.20	0.36	0.84	1.80	1.16	0.64	0.52	0.34	0.58	$H/2$	Water
A	Ethyl	2.48	0.88	1.60	0.52	0.40	0.12	0.01	0.04	0.20	$H^2/4$	Organic solvents

			6-	2-	3-		2-	3-	6-
		D.S.	X_6	X_2	X_3	Total	H	H	P
A	Ethyl	2.48	0.88	0.85	0.75	0.52	0.15	0.25	0.12

Substituents
(1) Sample.
(2) Substituent group.
(3) Degree of substitution.
(4) 6-Substitution.
(5) 2-, and 3-Substitution.

Unsubstituted groups
(6) Total hydroxyls.
(7) 2-, and 3-Hydroxyls.
(8) 6-Hydroxyls.
(9) 2,3-Glycol.

(10) Calculated for homogeneous.
(11) Calculated for heterogeneous.
(12) Glycol count.
(13) Solubility at 0°C.

tions of the cellulose did not react beyond the initial alkali-soluble stage and would not become organosoluble at any degree of substitution.

Timell[23] prepared and analyzed cellulose ethers from alkali cellulose, from sodium cupricellulose, and from cellulose in a quaternary base. His data are collected in Table 17. Methyl celluloses from alkali cellulose (A and B) were heterogeneous. Methyl celluloses from sodium cupricellulose (Table 15) had no substitution in the 6- position until above D.S. 1.1. Methyl cellulose, ethyl cellulose, *n*-propyl cellulose, and isopropyl cellulose were substituted homogeneously in quaternary bases.

Carboxymethyl cellulose and sulfoethyl cellulose appeared to approach homogeneous substitution, although the data were difficult to interpret. These ethers seemed to be substituted on one or the other of the secondary hydroxyls of a glucopyranose unit, but not on both. This may have been due to steric hindrance or to negative polarization of the residual hydroxyl of a 1,2-glycol pair. Dyer and Arnold[102] found that the *glycol count* of two different carboxymethyl cellulose samples was intermediate between that calculated for homogeneous and for heterogeneous reaction, but Rydholm[103] concluded that the substitution was essentially homogeneous. The statistical calculations of Spurlin[68] are not applicable to the case in which substitution of one secondary hydroxyl interferes with that of the other. The proper formulas for this case are given in Section A of this Chapter IX. It has been shown[104] that the distribution of substituents in carboxymethyl cellulose conforms to the revised calculations.

The micropreparation of 2-ethyl cellulose was claimed by Sugihara and Wolfrom,[105] who used copper to render unreactive the 6- position, regenerated cellulose (dehydrated azeotropically) to improve accessibility, and methyl iodide to secure slow diffusion and steric hindrance.

The substituent distribution in hydroxyalkyl celluloses is only partially known. Table 18 shows the data of Morgan,[33] who first published values of M.S., the moles of ethylene oxide consumed that become attached to the glucopyranose unit and to its substituent chains in hydroxyethyl cellulose.

The reaction of a mole of ethylene oxide with a secondary hydroxyl of a glucopyranose residue results in the conversion of one secondary hydroxyl to a primary hydroxyl:

[102] E. Dyer and H. E. Arnold, *J. Am. Chem. Soc.*, **74,** 2677 (1952).

[103] S. Rydholm, *Svensk Papperstidn.*, **53,** 561 (1950).

[104] T. Timell, *Svensk Papperstidn.*, **55,** 649 (1952); T. Timell and H. M. Spurlin, *Svensk Papperstidn.*, **55,** 700 (1952); **56,** 311 (1953).

[105] J. M. Sugihara and M. L. Wolfrom, *J. Am. Chem. Soc.*, **71,** 3509 (1949).

TABLE 17

Substituent Distribution in Cellulose Ethers (Timell[23])

(1)	(2)	(3)	(4) X_6	(5) $G_{2,3}$	(6) S_0	(7) S_2	(8) S_3	(9) S_6	(10) $S_{2,3}$	(11) $S_{2,6}$	(12) $S_{3,6}$	(13) $S_{2,3,6}$	(14) X_2+X_3	(15) $H^2/4$	(16) $H/2$	(17)
A	Methyl[a]	1.09	0.46	0.68	0.26	0.01	0	0	0.28	0	0	0.03	0.62	0.48	0.69	$H/2$
B	Methyl[b]	1.93	0.61	0.27	0.05	0	0	0.22	0.34	0.15	0	0.24	1.32	0.12	0.34	$H/2$
C	*n*-Propyl[c]	0.73	0.27	0.61	—	—	—	—	—	—	—	—	0.46	0.59	0.77	$H^2/4$
D	Isopropyl[d]	0.94	0.45	0.57	—	—	—	—	—	—	—	—	0.50	0.55	0.75	$H^2/4$
E	Carboxymethyl[e]	0.58	0.08	0.56	—	—	—	—	—	—	—	—	0.50	0.56	0.75	$H^2/4$
F	Sulfoethyl[f]	0.35	0.23	0.88	—	—	—	—	—	—	—	—	0.12	0.88	0.94	$H^2/4$

(1) Sample.
(2) Cellulose ether.
(3) Degree of substitution.
(4) 6-Substitution.
(5) 2,3-Glycol.
(6) Unsubstituted.
(7) 2-Substitution.
(8) 3-Substitution.
(9) 6-Substitution.
(10) 2,3-Substitution.
(11) 2,6-Substitution.
(12) 3,6-Substitution.
(13) 2,3,6-Substitution.
(14) 2-, and 3-Substitution.
(15) Calculated for homogeneous.
(16) Calculated for heterogeneous.
(17) Glycol count.

[a] Sulfite pulp, 35% NaOH, methyl sulfate; soluble in cold water.
[b] Commercial, U.S.A.; soluble in cold water.
[c] Viscose, quaternary base, *n*-propyl bromide (IV); solubility not given.
[d] Viscose, quaternary base, isopropyl bromide (III); soluble in pyridine (at D.S. 0.73, soluble in water)
[e] Commercial, U.S.A.; soluble in water.
[f] Cellulose, NaOH, sodium β-chloroethylsulfonate; soluble in cold water.

$$\mathrm{R_{cell}CHOH} + \underbracket{\mathrm{CH_2CH_2O}} \longrightarrow \mathrm{R_{cell}CHOCH_2CH_2OH} \tag{2}$$

The number of initial primary hydroxyls remains unchanged:

$$\mathrm{R_{cell}CH_2OH} + \underbracket{\mathrm{CH_2CH_2O}} \longrightarrow \mathrm{R_{cell}CH_2OCH_2CH_2OH} \tag{3}$$

The number of primary hydroxyls also remains unchanged when chain growth takes place:

$$\mathrm{R_{cell}CH_2OCH_2CH_2OH} + \underbracket{\mathrm{CH_2CH_2O}} \longrightarrow \mathrm{R_{cell}CH_2OCH_2CH_2OCH_2CH_2OH} \tag{4}$$

TABLE 18

Analyses of Hydroxyethyl Cellulose (Morgan[33])

Moles ethylene oxide used per glucopyranose unit	M.S.	Efficiency, %	Solubility
0.25	0.17	68	7% NaOH
Commercial	0.18	—	7% NaOH
Commercial	0.23	—	7% NaOH
0.50	0.25	51	7% NaOH
0.75	0.42	57	Swollen by cold water
1.50	0.73	48	Swollen by many solvents but not by acetone
Commercial	1.44	—	Soluble in water, nearly soluble in acetic acid or pyridine
4.05	1.84	46	Soluble in water, acetic acid, or pyridine
10.0	4.10	41	Soluble in water and in aqueous ethanol, but not in acetone

Tasker and Purves[106] and Cohen and Haas[107] published partial analyses of hydroxyethyl cellulose. The results of Cohen and Haas for four samples of variant substitution are shown in Table 19.

TABLE 19

Analyses of Hydroxyethyl Cellulose (Cohen and Haas[107])

Sample	M.S.	2,3-Glycol, $G_{2,3}$	Primary hydroxyls formed $(1 - G_{2,3})$	Primary hydroxyls	Ethylene oxide loss on extended tosylation
I	0.44	0.71	0.29	—	—
II	0.97	0.57	0.43	—	—
III	1.50	0.48	0.52	1.46	0.84
IV	3.07	0.34	0.66	—	—

[106] C. W. Tasker and C. B. Purves, *J. Am. Chem. Soc.*, **71**, 1023 (1949).

[107] S. G. Cohen and H. C. Haas, *J. Am. Chem. Soc.*, **72**, 3954 (1950).

The data from sample III of Cohen and Haas[107] (Table 19) indicate that one glycol group ($G_{2,3}$) was used for each new primary hydroxyl that was formed. It was concluded that sample III appeared to have 50% of its glucopyranose units substituted in either the 2- or the 3- position, to have 50% of its glucopyranose residues not substituted on the 2- or the 3- position (the glycol group $G_{2,3}$ was still present), and to have no glucopyranose units substituted on both the 2- and 3- positions.

TABLE 20

Arbitrary Compositions of Hydroxyethyl Cellulose[106,107; see also 23,108]

			Ethylene oxide substitution per mole			
			Primary		Secondary	
Sample	M.S.	D.S.	Mono-	Di-	Mono-	Di-
Tasker and Purves[106]	0.44	0.37	0.13	0.02	0.17	0.05
Cohen and Haas,[107] I[a]	0.44	0.37	0.06	0.02	0.24	0.05
Cohen and Haas,[107] III[a]	1.50	0.94	0.10	0.34	0.28	0.22

[a] See Table 19.

If it is assumed that the length of the polyethylene oxide chains did not exceed D.P. 2 in samples I and III of Cohen and Haas and in the sample (similar to I) of Tasker and Purves, the arbitrary compositions shown in Table 20 may be calculated on the basis of their 3- to 5-hr. tosylation–halogenation data.[23,108]

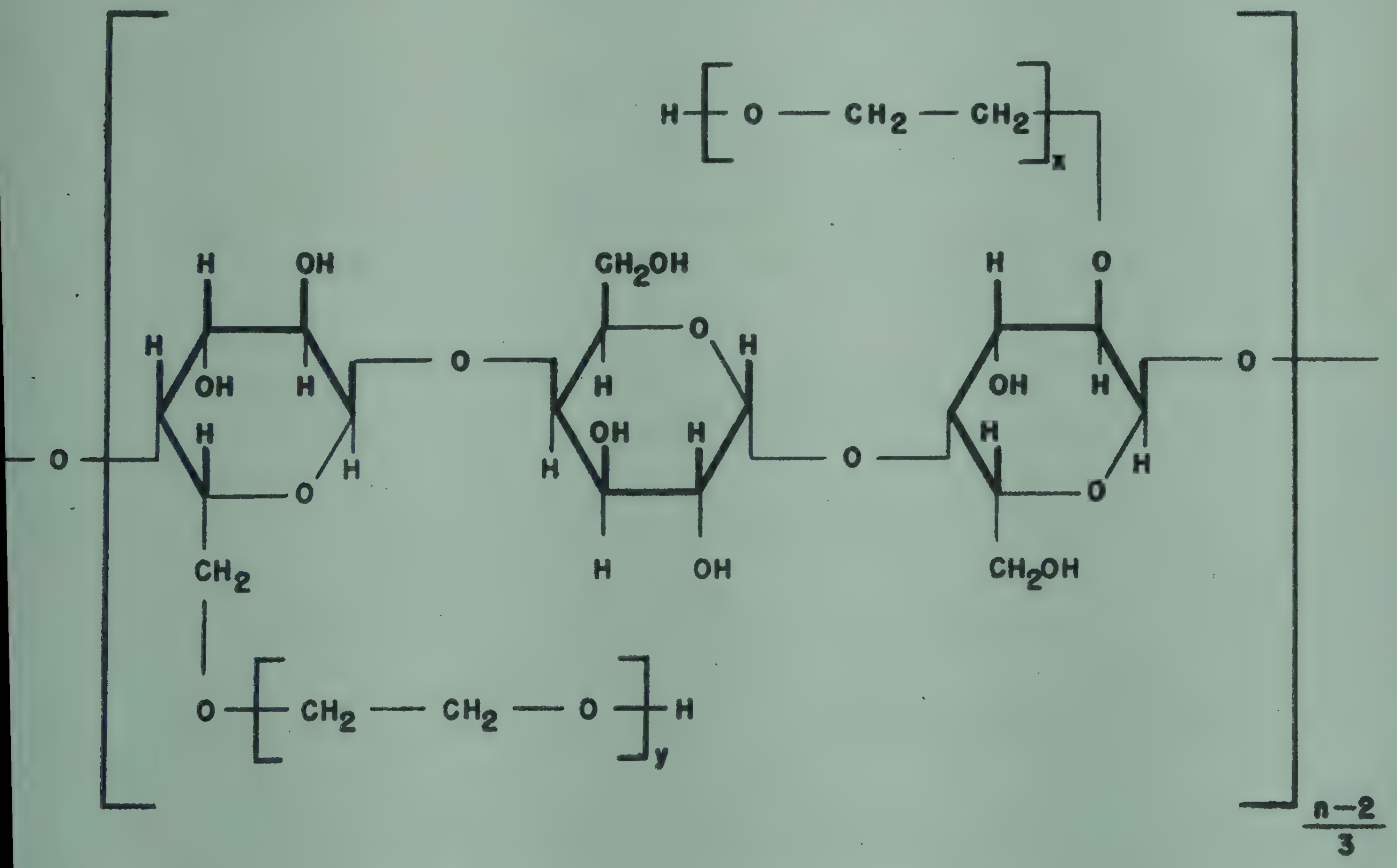

Fig. 59. Structure of hydroxyethyl cellulose.

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[108] J. F. Mahoney and C. B. Purves, *J. Am. Chem. Soc.*, **64**, 9 (1942).

As the M.S. increased, the polyethylene oxide chains increased in length. Morgan[33] pointed out that hydroxyethyl celluloses, unlike other cellulose ethers, showed increasing solubility in all media with increasing substitution. Thus water solubility produced by the wedging apart of the cellulose chains by hydroxyethoxyl substitution was not lost when the extended polyethylene oxide chains produced organosolubility.

Hydroxyethyl cellulose is of the structural type shown in Figure 59.

(f) FRACTIONATION OF ETHYL CELLULOSE

The analyses of cellulose ethers that have been presented are average values for experimental or for commercial products; they do not take into account the variation in composition of the samples. Since the initial cellulose is a random mixture of molecules of diverse size and its breakdown by cleavage is likewise random,[109] it is not surprising that cellulose ethers are random mixtures of molecules that differ from one another in both substitution and size.

The properties that best describe a particular cellulose ether are its degree of substitution and its viscosity. In practice, the viscosities of solutions of finite concentration determine commercial utility, but from a theoretical point of view the limiting or *intrinsic viscosity* (limit of η_{sp}/c as c approaches zero) better describes the average length of a molecule (see Chapter XII-A). Suitable factors for the conversion of intrinsic viscosity values to numerical degrees of polymerization for cellulose ethers are not available in the literature, because closely fractionated samples of uniform D.S. and D.P. have not been prepared. The determination of intrinsic viscosity has been discussed in part by Davis and Elliott.[110]

If a cellulose ether is to be completely described, it must be fractionated and each fraction must be analyzed both for substitution and for intrinsic viscosity.

The customary technique of solvent precipitation is particularly applicable to ethyl cellulose. Okamura[111] dissolved ethyl cellulose in acetic acid and precipitated fractions by adding water. Staudinger and Reinecke[112] used dioxane and water. Ushakov and Geller[113] used alcohol and gasoline. Scherer and McNeer[114] tried the systems benzene and *n*-heptane, and acetone and water unsuccessfully. They also used acetic acid–water, but failed to stabilize their products. They finally used ethyl acetate–acetone as the solvent and acetone–water as the nonsolvent. Barry[19] used chloroform as the solvent and petroleum ether (Skellysolve, b. p. 100–140°C.) as the nonsolvent. Samsel and Warren[19] used chloroform as the solvent and petrobenzol[115] as the nonsolvent. Scherer and Iacoviello[116] used benzene–methanol as the solvent and heptane–benzene as the nonsolvent.

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[109] G. Beall and L. Jörgensen, *Textile Research J.*, **21**, 203 (1951).

[110] W. E. Davis and J. H. Elliott, *J. Colloid Sci.*, **4**, 313 (1949). See also Chapter X-F of this book.

[111] I. Okamura, *Cellulosechemie*, **14**, 135 (1933).

The course of a fractionation will depend upon the nature of the solvents and the precipitants used, but in general the material of high molecular weight will be precipitated first.

If the ethyl cellulose is dissolved in a solvent such as chloroform, and if to this mixture is added a nonpolar liquid such as petroleum ether, material of low degree of substitution will be precipitated first; as the solvent mixture is made less active, the degree of substitution of the fractions obtained will gradually increase. If, on the other hand, the ethyl cellulose is dissolved in alcohol and water is then added, the first fractions precipitated will be high in degree of substitution, and the low-substituted material will remain in solution.

If the determined degree of substitution of a sample is rather high (above 2.5, for example), there can be relatively little low-substituted material present. If, in addition, the intrinsic viscosity is relatively high, fractionation will be by chain length rather than by degree of substitution. Thus, Staudinger and Reinecke[112] and Scherer and McNeer[114] found a narrow degree-of-substitution range in the fractionation of high-intrinsic-viscosity ethyl cellulose of D.S. 2.6.

Scherer and Iacoviello[116] fractionated ethyl celluloses of D.S. 2.54 and

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[112] H. Staudinger and F. Reinecke, *Ann.*, **535**, 47 (1938).

[113] S. N. Ushakov and I. M. Geller, *Plasticheskie Massui Sbornik Statel*, **30**, (1939); through P. C. Scherer and R. D. McNeer, *Rayon and Synthetic Textiles*, **30**, No. 8, 56 (1949); **31**, No. 2, 53 (1950); **31**, No. 4, 54 (1950).

[114] P. C. Scherer and R. D. McNeer, *Rayon and Synthetic Textiles*, **30**, No. 8, 56 (1949); **31**, No. 2, 53 (1950); **31**, No. 4, 54 (1950).

[115] Petrobenzol is an aliphatic naphtha, manufactured by Anderson Prichard Oil Co., and described in H. A. Gardner, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, 9th ed., Inst. of Paint & Varnish Research, Washington, D. C., 1939, p. 570.

[116] P. C. Scherer and J. G. Iacoviello, *Rayon and Synthetic Textiles*, **32**, No. 11, 47 (1951).

2.23. They obtained a high degree of reproducibility of their technique and report a wide range of D.P. within the samples.

Samsel and Warren[19] fractionated ethyl cellulose of D.S. 2.4 and found a range of 0.1 to 0.2 D.S. in the recovered fractions; these data are shown in Table 21. The total distribution within the original samples is not described completely by the mean, range, and standard deviation[117] of the fractions, however, because the recovery was only about 90%.

TABLE 21

Fractionation of Ethyl Cellulose, D.S. 2.4 (Samsel and Warren[19])

Sample batch	Determined D.S.	Fractions			Intrinsic viscosity[a]
		Mean D.S.	Range	Standard deviation	
A	2.42	2.41	0.21	0.065	1.75
B	2.46	2.43	0.18	0.066	1.7
C	2.41	2.31	0.23	0.083	1.8
D	2.40	2.34	0.18	0.054	1.8
E	2.38	2.34	0.18	0.077	2.0
F	2.38	2.34	0.19	0.076	2.0
G	2.43	2.38	0.18	0.066	2.1
H	2.40	2.36	0.10	0.036	2.11

[a] Intrinsic viscosity solvent: 70:30 benzene:methanol.

Few fractionations of other cellulose ethers have been reported. Methyl celluloses were fractionated by Signer and von Tavel[118] and by Steele and Pacsu.[119] Timell and Purves[120] nitrated alkali-soluble methyl celluloses by a nondegradative method. The trisubstituted portions of nonuniform methyl cellulose dissolved in the nitrating mixture. The resultant products were subjected to fractional precipitation and fractional solution on a micro scale. The methoxyl degrees of substitution of the fractions varied inversely as their viscosities. The alkali-soluble methyl celluloses became more uniform in this respect as their degrees of substitution increased. Alkali-soluble methyl celluloses prepared with methyl chloride[121] were more uniform than similarly substituted methyl celluloses[120] prepared with methyl sulfate.

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[117] K. A. Brownlee, *Industrial Experimentation*, 3d American ed., Chemical Publishing Co., Brooklyn, N. Y., 1949, p. 26.

[118] R. Signer and P. von Tavel, *Angew. Chem.*, **50**, 902 (1937); **51**, 535 (1938).

[119] R. Steele and E. Pacsu, *Textile Research J.*, **19**, 771, 784 (1949).

[120] T. Timell and C. B. Purves, *Svensk Papperstidn.*, **54**, 303 (1951).

[121] A. T. Maasberg (to The Dow Chemical Co.), U. S. Patent 2,408,326 (Sept. 24, 1946); *Chem. Abstracts*, **41**, 1104 (1947).

3. Properties of Cellulose Ethers

(a) THE SOLUBILITY OF CELLULOSE ETHERS

A given cellulose ether is most soluble in solvents that best match the ether or its solvated derivative in cohesive energy density.[122] When a cellulose ether is prepared, the gradual increase in degree of substitution of the ether is accompanied by a transition from insoluble cellulose through solubility in the following series of solvent types: aqueous alkali, water, water–alcohol mixtures, hydrocarbon–alcohol mixtures or equivalent solvents, and finally aromatic hydrocarbons. The solubility in water and other hydroxylic solvents is generally lost as solubility in hydrocarbon solvents is reached.

The variation of solubility of cellulose ethers with degree of substitution is shown in Table 22. Ethyl cellulose and, to a lesser extent, methyl cellulose go through the stages outlined. The higher aliphatic ethers, propyl cellulose and butyl cellulose, are not very soluble in aqueous alkali or in water at any time, but isopropyl cellulose prepared in a homogeneous manner was found by Timell[23] to be water-soluble. Benzyl cellulose made from fibrous alkali cellulose is not soluble in alkali or in water at any stage.

Sodium carboxymethyl cellulose does not pass beyond the water–alcohol-soluble stage. The heavy metal salts of carboxymethyl cellulose are soluble only in aqueous alkali. The free acid form, as commonly made by acidification, is also soluble only in aqueous alkali, but conversion of an aqueous solution of the sodium salt by means of ion-exchange resins yields a water dispersion of carboxymethyl cellulose that becomes water-insoluble when dried. Table 22 likewise shows that ethers prepared homogeneously (samples B) from sodium cupricellulose or in quaternary bases are soluble at lower degrees of substitution than are the corresponding ethers prepared from alkali cellulose (samples A).

Swelling is considered to be solution of the solvent in the cellulose ether; there is thus little difference between a swollen gel and a solution. An ether may be swelled by a solvent at degrees of substitution both above and below the degree of substitution at which it is soluble in the solvent.

Ethers of a given degree of substitution are more soluble, the lower their intrinsic viscosity is; degraded cellulose ethers are more soluble than are undegraded ethers of the same kind.

The solubility of low-substituted ethers in 4 to 10% NaOH solution is greater near 0°C. than at higher temperatures. Chilling apparently aids the hydration of the cellulose hydroxyls. Water solubility is held to result

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[122] H. M. Spurlin, *J. Polymer Sci.*, **3**, 714 (1948).

TABLE 22

Variation of Solubility of Cellulose Ethers with Degree of Substitution[a]

Solubility stage	Methyl cellulose, D.S.		Ethyl cellulose, D.S.	
	A	B	A	B
1. 4 to 8% NaOH	0.1[123] 0.2–0.4[124] 0.4–0.6[8,84,125,126]	0.1[72]	0.5–0.7[84,125]	
2. Cold water	1.3–2.6[8,19,127,129]	1.0[23] 1.1[72]	0.7[19] 0.8–1.3[84,125]	0.5[22] 0.6[84]
3. Increasing in alcohol	2.1–2.6[19]	—	1.4–1.8[125,128]	1.1–1.4[22]
4. Increasing in solvents	2.4–2.7[19]	—	1.8–2.2[125,128]	
5. Increasing in hydrocarbons	2.6–2.8[19]	—	2.7–2.9[19]	

	Propyl cellulose, D.S.			Butyl cellulose, D.S.	Benzyl cellulose, D.S.
	normal-		iso-		
	A	B	B	A	A
2. Cold water	—	—	0.5[23]		
3. Increasing in alcohol	—	0.5[22]	—		
4. Increasing in solvents	1.5[19,130]	—	—	0.6–1.0[22]	
5. Increasing in hydrocarbons	1.8[19]	—	—	1.8–2.0[19]	1.8[19]

	Sodium carboxymethyl cellulose, D.S.	Hydroxyalkyl cellulose, M.S.
	A	A
1. 4 to 8% NaOH	0.05–0.25[19]	0.25[19,33]
2. Cold water	0.3–0.8[19]	1.5–2.5[131,132] 1.4[33]
3. Increasing in alcohol	2.0–2.8[32]	1.6–2.6[33]

[a] Sample A, from alkali cellulose; sample B, from sodium cupricellulose or quaternary base.

from the wedging apart of the cellulose chains by the substituent groups, so that the remaining hydroxyls are available for hydration.[133] Bulky substituent groups enable water solubility to be obtained at lower degrees of substitution than is the case with the less bulky methyl or ethyl groups. Thus methyl cellulose is water-soluble at D.S. 1.3, ethyl cellulose at D.S. 0.7, isopropyl cellulose at D.S. 0.5, and sodium carboxymethyl cellulose at D.S. 0.5. Hydroxyethyl cellulose is water-soluble at D.S. 0.8 (see Tables 18 and 20) or M.S. 1.4. It is interesting to note that water solubility occurs at about the same weight per cent of added substituent in all these cases.

Solubility in organic solvents stems from predominance of the substituent groups over the remaining hydroxyl groups. The best solvents most closely resemble the cellulose ethers, and, in general, alcohol–hydrocarbon mixtures are better solvents than are single solvents. The maximum over-all solubility is reached at a substitution of less than D.S. 3.0. Thus ethyl cellulose is most soluble in alcohol–hydrocarbon mixtures at D.S. 2.4 to 2.5 and becomes decreasingly soluble in alcohols as D.S. increases. Ethyl cellulose of D.S. 2.7 to 2.9 is dispersible in aromatic hydrocarbons.

The proportion of alcohol that must be used in alcohol–hydrocarbon solvent mixtures to obtain minimum viscosity is proportional to the number of hydroxyls that remain unsubstituted in the cellulose ether. Thus ethyl cellulose of D.S. 2.2 requires 70:30 benzene:methanol to dissolve it, whereas ethyl cellulose of D.S. 2.6 is soluble in 95:5 benzene:methanol or in 80:20 toluene:ethanol, and ethyl cellulose of D.S. 2.8 is dispersed in benzene or toluene alone. Better film properties are obtained if the amount of alcohol slightly exceeds these minimum values.

[123] J. F. Haskins and R. W. Maxwell (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,131,733 (Oct. 4, 1938); *Chem. Abstracts*, **32**, 9496 (1938).

[124] D. C. Ellsworth and F. C. Hahn (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,157,530 (May 9, 1939); *Chem. Abstracts*, **33**, 6595 (1939); U. S. Patent 2,249,754 (Jan. 22, 1941); *Chem. Abstracts*, **35**, 7190 (1941).

[125] E. J. Lorand, *Ind. Eng. Chem.*, **30**, 527 (1938).

[126] L. Lilienfeld, U. S. Patent 1,589,606 (June 22, 1926); *Chem. Abstracts*, **20**, 3084 (1926).

[127] E. Heuser and W. von Neuenstein, *Cellulosechemie*, **3**, 89 (1922).

[128] E. Berl and H. Schupp, *Cellulosechemie*, **10**, 41 (1929).

[129] H. Staudinger and O. Schweitzer, *Ber.*, **63B**, 2327 (1930).

[130] S. N. Ushakov and S. I. Kucherenko, *Plasticheskie Massy*, **3**, 12 (1934).

[131] A. W. Schorger (to Burgess Laboratories), U. S. Patent 1,863,208 (June 14, 1932); *Chem. Abstracts*, **26**, 4174 (1932); U. S. Patent 1,914,172 (June 13, 1933); *Chem. Abstracts*, **27**, 4243 (1933); U. S. Patents 1,941,276, 1,941,277, and 1,941,278 (Dec. 26, 1933); *Chem. Abstracts*, **28**, 1861 (1934).

[132] A. W. Schorger and M. J. Shoemaker, *Ind. Eng. Chem.*, **29**, 114 (1937).

[133] F. D. Farrow and S. M. Neale, *J. Textile Inst.*, **15**, T157 (1924).

(b) THE GELATION OF WATER-SOLUBLE CELLULOSE ETHERS

Homogeneously prepared water-soluble methyl cellulose and water-soluble ethyl cellulose dissolve to give aqueous solutions that can be heated to near their boiling points without gelation.[19] Such nongelling ethers have been prepared from alkali cellulose, from sodium cupricellulose, and from reaction in quaternary bases. These preparations are characterized by their water solubility at lower degrees of substitution than hold for the corresponding heterogeneously prepared ethers. It is believed that their failure to gel upon heating is due to lack of trisubstitution,[134] but it is also possible that freedom from long unaltered residues of the original cellulose structure is the important factor. Solutions of heterogeneously prepared ethers gel from solution upon heating.

The reversible gelation of a methyl cellulose of D.S. 2.22 was studied by Heymann,[135] who called the gelation of this methyl cellulose upon heating an *inverse* transformation to distinguish it from the gelation upon cooling that is observed in solutions of agar-agar and gelatin. The viscosity of a given solution of methyl cellulose decreased as the temperature of the solution was increased. Heymann attributed this to a decrease in hydration of the methyl cellulose that accompanied the rise in temperature. As the gel point was approached, small increments of temperature produced large increases in viscosity; maintenance of the solution viscosity required an increased rate of shear to break down the gels that formed. When the gelation temperature was reached, the application of shearing force could no longer maintain the solution state, the viscosity rose rapidly, and a large aggregate of gel separated from the water. When the gelled solution was cooled, the viscosity returned to its original value by a direct path.

The gelation temperature decreased with increasing concentration of methyl cellulose of a given viscosity. When the concentration was fixed, the gel temperature decreased with increasing viscosity of the methyl cellulose. At low concentrations, or with methyl cellulose of low viscosity, turbidity was obtained, rather than actual gelation. This turbidity was due to gel particles.

The presence of soluble inorganic salts in methyl cellulose solutions generally lowered the gelation temperature by decreasing the hydration of the methyl cellulose. High concentrations of salt caused gelation at room temperature. The salt concentration that a solution could tolerate decreased with increasing methyl cellulose concentration and decreased with increased viscosity of the methyl cellulose. The effect of salt addition was similar to

[134] J. Vacher, *Chimie & industrie,* **43,** 347 (1940).

[135] E. Heymann, *Trans. Faraday Soc.,* **31,** 846 (1935); **32,** 462 (1936).

the effect of heating. The salt tolerance depended upon the ions present: Soluble thiocyanates and iodides raised the gelation temperature; other ions lowered it in the order phosphate > sulfate > tartrate > acetate > chloride > nitrite > nitrate. This is the familiar lyotropic series of ions.

Gelation is a very slow process at temperatures just below the gel point, which indicates that the chains require time to diffuse to the required positions for association.

(c) THE THERMOPLASTICITY OF CELLULOSE ETHERS

The thermoplastic properties of cellulose ethers at elevated temperatures may be looked upon as an extension of their solution properties, for the degree of substitution at which maximum solubility is obtained is also that of the lowest softening or flow temperature of the cellulose ether.

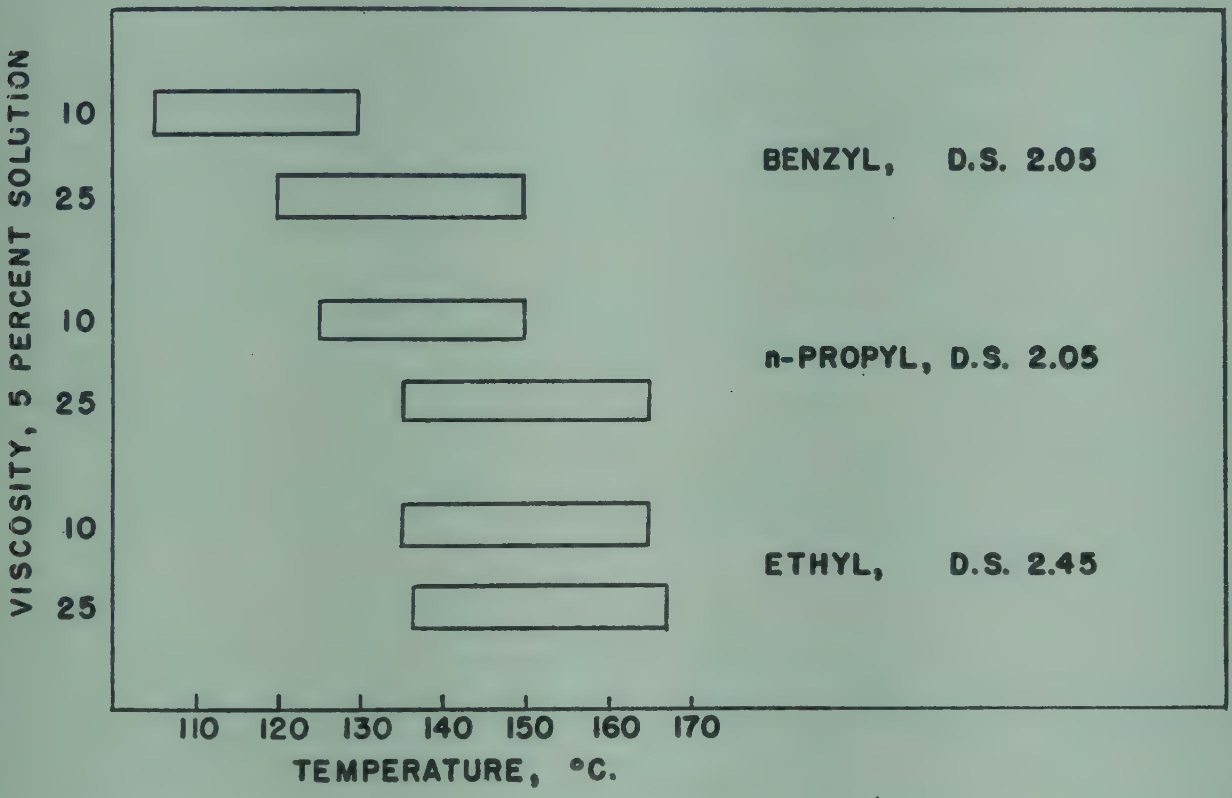

Fig. 60. Softening–melting point ranges of benzyl cellulose, *n*-propyl cellulose, and ethyl cellulose; viscosity in cps. (The Dow Chemical Co.[19]).

The thermoplasticity of a cellulose ether depends upon the nature of its substituent group, the degree of substitution, and the chain length of the ether. The softening temperature decreases as the substituent size increases: Thus methyl cellulose softens at over 190°C., whereas ethyl cellulose of similar substitution softens near 140°C.

Figure 60 shows the effect of the nature of the substituent group upon the softening–melting point range for some cellulose ethers prepared from alkali cellulose and alkyl chlorides by Savage.[19] Ethyl cellulose of D.S. 2.42

was similar in softening temperature to *n*-propyl cellulose of D.S. 2.05. These ethers softened at 125° to 135°C.; ethyl cellulose of D.S. 2.05 would soften only above 170°C. Benzyl cellulose of D.S. 2.05 softened at 105° to 120°C. The softening points of benzyl cellulose and *n*-propyl cellulose approached that of ethyl cellulose as the viscosity increased from 10 to 25 cps. The softening and melting points were determined for sheeting on a modified Dennis-Shelton[136] melting-point bar. Lorand[125] reported lower softening points for benzyl cellulose.

The softening temperature of a cellulose ether of a given degree of substitution is higher, the higher the intrinsic viscosity of the ether. This is shown for ethyl cellulose[137] in Table 23.

TABLE 23

The Effect of Intrinsic Viscosity upon the Softening Temperature of Ethyl Cellulose of D.S. 2.45 (Hercules Powder Company[137])

Intrinsic viscosity[a]	5% Solution[a] viscosity, cps.	Softening temperature, °C.[b]
0.8–0.9	7–9	151
1.0–1.3	13–20	156
1.6	42.5	161
2.1	93.5	167
2.8	199	171

[a] Intrinsic viscosity and 5% viscosity solvent: 80:20 toluene:ethanol.
[b] Penetration softening point.[137]

Small quantities of cellulose ethers dissolve in large amounts of the common solvents at room temperature or below. The concentration that can be reached depends upon the chain length of the cellulose ether and upon the solvent used. As the concentration of the ether is increased, portions of the ether no longer dissolve well (the solvent becomes saturated with respect to certain fractions) and the apparent viscosity of the solution is greatly increased. (The ratio of the viscosity in such a medium at a high concentration to the viscosity of, for example, a 5% solution is termed the *viscosity index;* it is a measure of the solvent power on the one hand and of the uniformity of substitution of the ether on the other hand.) If now the temperature is raised, the viscosity index is decreased; the amount of the cellulose ether dissolved may be increased and the amount of the solvent may be decreased. As the temperature is raised higher, a state of concentration is ultimately reached that amounts to solution of the solvent in the cellulose ether. The cellulose ether swelled by the solvent resembles a liquid in its properties.

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[136] L. M. Dennis and R. S. Shelton, *J. Am. Chem. Soc.*, **52**, 3128 (1930).
[137] *Ethyl Cellulose*, Hercules Powder Co., Wilmington, Del., 1949.

If the product is to be technically useful, it must reassume a certain degree of hardness when its forming by fluid flow or by plastic flow has been completed. This depends upon applying the right conditions of temperature and pressure to the swelled cellulose ether, which must have been formulated to give the desired end properties.

The agents that are used to modify a cellulose ether during plastic forming or to impart particular properties to a finished form of the cellulose ether are called plasticizers. If a permanent effect is desired, a nonvolatile, stable plasticizer must be used. Cellulose ethers are compatible with a variety of different plasticizing compounds, but the more effective plasticizers closely resemble in structure the cellulose ether with which they are used. Thus water-soluble ethers are plasticized by hydroxyl-containing compounds such as glycols; esters or ethers are suitable for cellulose ethers of intermediate substitution; nonsolvent oils may be used to plasticize highly substituted ethers.

Each cellulose ether may be considered to be, in a sense, internally plasticized by its substituent group; thus benzyl cellulose may be molded without an added plasticizer. The internal plasticization is greater, the lower the yield point is. Table 24 shows the yield points of several cellulose ethers.

TABLE 24

Internal Plasticization of Cellulose Ethers Shown by Their Yield Points (The Dow Chemical Company[19])

Cellulose ethers	D.S.	Yield point, kg./sq. cm.[a]
Methyl cellulose	2.0	600
Methyl cellulose	2.8	525
Ethyl cellulose	2.3	510
Ethyl cellulose	2.5	475
n-Propyl cellulose	1.5	375
Butyl cellulose	1.8	275
Amyl cellulose	1.8	100
Benzyl cellulose	2.0	390

[a] Yield point from load–elongation curves on sheeting tested in Scott tensile strength tester at 5-kg. load and loading rate of 25.4 mm./min.

The internal plasticization is proportional to the size of the substituent group. Such substituent groups as hydroxyethyl and hydroxypropyl are increasingly effective as internal plasticizers as their side chains increase in length.

(d) THE MECHANICAL PROPERTIES OF CELLULOSE ETHERS

The mechanical properties of a cellulose ether depend upon the plasticization, whether internal (by substitution) or external (by an added plasticizer), and upon the intrinsic viscosity of the cellulose ether.

The relation of intrinsic viscosity to the mechanical properties of ethyl cellulose[137] is shown in Table 25. The tensile strength, flexibility, and elongation increase with viscosity, provided that fibers and gels are absent. Both tensile strength and elongation vary with the casting solvent used.

TABLE 25

The Effect of Intrinsic Viscosity on the Physical Properties of Ethyl Cellulose of D.S. 2.45 (Hercules Powder Company[137])

Intrinsic[a] viscosity	Solution viscosity, 5% solution, cps.[a]	Sheeting[a] thickness, in.	Yield point, lb./sq. in.[19]	Tensile strength, lb./sq. in.	Flexibility by Schopper double folds
0.85	7.4	0.0031	—	7960	17
0.93	9.3	0.0030	6500	7670	23
1.05	13.0	0.0030	—	8100	42
1.25	19.7	0.0030	7800	8250	65
1.62	42.5	0.0030	—	8390	90
2.15	93.5	0.0030	8800	9100	128
2.80	199	0.0030	—	9240	248

[a] Intrinsic viscosity, 5% viscosity, and casting solvent: 80:20 toluene:ethanol.

The moisture sorption of a cellulose ether depends upon the number of free hydroxyl groups and upon the size and the nature of the substituent group, as shown in Table 26.

TABLE 26

Effect of Substituent Group on the Moisture Sorption of Cellulose Ethers (Lorand[125])

Cellulose ether	D.S.	Softening[a] temperature, °C.	Moisture sorption, % at 72% relative humidity and 19°C.
Ethyl cellulose	2.15	158	3.0
Butyl cellulose	2.28	65	1.7
Amyl cellulose	1.91	45	1.0

[a] Penetration softening point.[137]

Figure 61 shows that the moisture sorption of ethyl cellulose decreases with increasing degree of substitution and increases with increasing relative humidity, but is less in water at 50°C. than in water at 21°C.

Table 27 shows the moisture vapor transmissions of some cellulose ether sheets in comparison to ethyl cellulose sheeting of comparable thickness as a standard, since the moisture vapor transmission values may vary considerably with the thickness of the sheeting.

The values of mechanical properties cited are rather general ones for typical ethers. It should be remembered that cellulose ethers are mixtures, both with respect to chain length and with respect to degree of substitution; here again, if the mechanical properties are to be completely described, the ether must be fractionated and the properties of the individual fractions must be determined.[114]

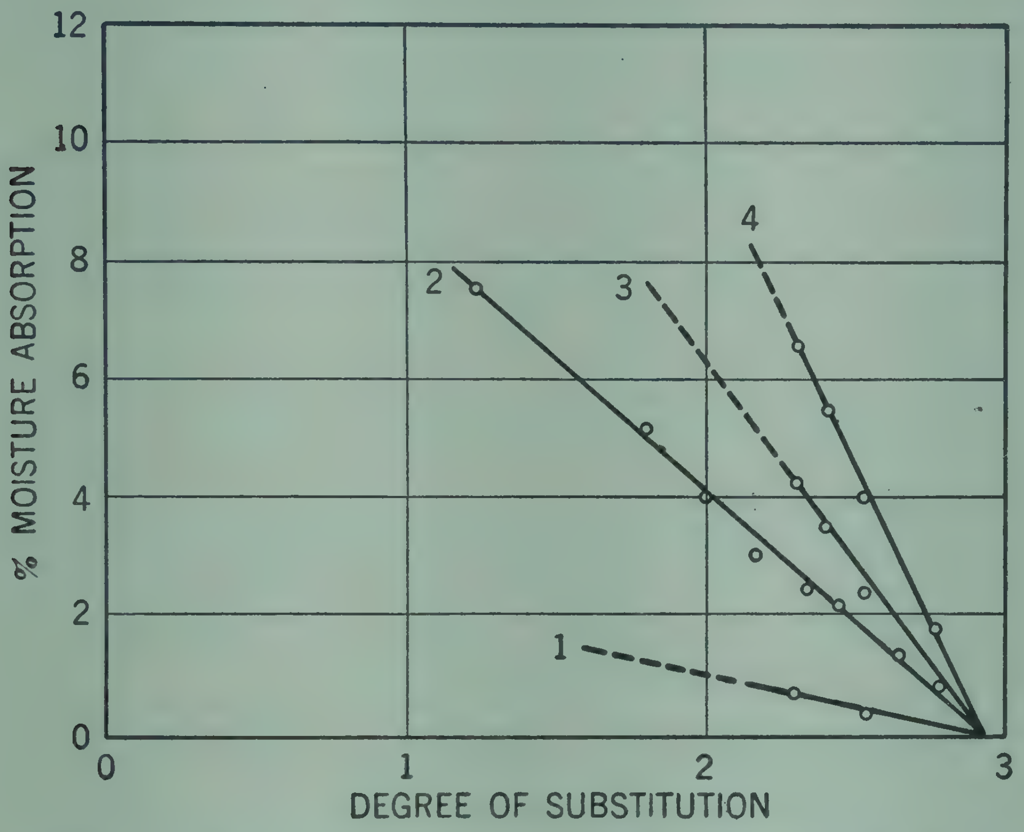

Fig. 61. Ethyl cellulose: relation of degree of substitution to moisture absorption (The Dow Chemical Co.[19]). Lines: *1*, 50% R.H., 21°C.; *2*, 70% R.H., 19°C.; *3*, water immersion, 50°C.; *4*, water immersion, 21°C.

4. Ethyl Cellulose

The uses of ethyl cellulose are many and varied. It is formulated into plastics, lacquers, transparent sheeting, melts, varnishes, and adhesives.

Ethyl cellulose is tough; it retains strength and flexibility over an extreme range of temperature. It is useful in both rigid and soft plastics, and can be fabricated by extrusion, injection molding, compression molding, drawing, and casting. Ethyl cellulose toughens and hardens most compositions in which it is compatible, it is soluble in many low-cost solvents, and it is compatible with a wide range of plasticizers and resins. It can be formulated for many varied uses; it can be tailored for the specific use.

Ethyl cellulose may be made in three ranges of substitution:

Commercial ethyl cellulose ranges in D.S. from 2.20 to 2.58 (ethoxyl content from 44.0 to 49.5%); it is soluble in common organic solvents and is thermoplastic.

TABLE 27

Effect of Degree of Substitution of Cellulose Ethers upon Water Vapor Transmission (Ronda[19])

Sheeting	D.S.	Thickness, in.	Water vapor transmission, g./100 sq. in./24 hr. Absolute	Water vapor transmission, g./100 sq. in./24 hr. Relative to ethyl cellulose, D.S. 2.4
Methyl cellulose	2.0	0.0025	72	219
Ethyl cellulose	2.4	0.0025	33	100 base
Ethyl cellulose	2.3	0.001	111	219
Ethyl cellulose	2.4	0.001	52	100 base
Ethyl cellulose	2.6	0.001	94	180
Ethyl cellulose	2.4	0.001	52	100 base
Benzyl cellulose	2.0	0.008	3	18
Ethyl cellulose	2.4	0.008	18	100 base

Nearly completely substituted ethyl cellulose ranges in D.S. from 2.60 to 2.80 (ethoxyl content 50.0 to 52.5%); it is soluble in hydrocarbons, but is not soluble in many of the common oxygenated solvents. It is limited in compatibility, and suitable plasticizers for its thermoplastic use have not been found. It is incompatible with the commercial ethyl cellulose of lower degree of substitution.

Low-substituted ethyl cellulose, ranging in D.S. from 0.8 to 1.7 (ethoxyl content 19 to 35%), is water-soluble. The control of ethylation to obtain water solubility is difficult.

Ethyl cellulose is prepared by the etherification of alkali cellulose with ethyl chloride, followed by the isolation, washing, and drying of the product. In this section the manufacture of ethyl cellulose of D.S. 2.20 to 2.58 is discussed in detail; the higher and lower substituted ethyl celluloses are briefly mentioned.

(a) RAW MATERIALS

The common sources of cellulose for ethylation are bleached and purified cotton linters and wood pulp. The sheet cellulose, commonly supplied in roll form, must be uniform in weight, density, water absorbency, and aqueous sodium hydroxide absorbency. It must be high in alpha-cellulose content, very low in incrustants, free of metals, free of knots or clots of fibers, and must not have been overdried. Typical analyses[138] of celluloses suitable for ethylation are shown in Table 28.

TABLE 28

Typical Celluloses Used in Ethylation (Martin[138])

	Chemical cotton	Wood pulp
Alpha-cellulose, %	98.7	94.5
Beta-cellulose, %	1.3	3.0
Gamma-cellulose, %	0	2.5
Moisture, %	6	6
Color, G.E. brightness	90	85
Ash, %	0.05	0.06
Iron, p.p.m.	12	12
Calcium, p.p.m.	50	50
Viscosity, TAPPI Standard T 230, 1% cupriethylenediamine, cps.	40	65

The ethyl chloride used is pure; it should contain less than 20 parts per million of sulfur and less than 50 parts per million of acetaldehyde. The sodium hydroxide must contain less than 40 parts per million of iron and must be very low in alkaline earth metals.

(b) PROCESSES

When alkali cellulose is etherified with ethyl chloride, at least one-half of the ethyl chloride that is consumed is converted to by-products, chiefly ethanol and ethyl ether. If other factors are equal, the ratio of ether to ethanol is greater, the longer the reaction time is.

The ethylation reaction is carried out either with excess sodium hydroxide and limited ethyl chloride, or with limited sodium hydroxide and excess ethyl chloride.

Ethylation efficiency is the percentage of the total ethyl chloride consumed that becomes substituent upon the cellulose. Efficiency is related both to the concentration and the amount of sodium hydroxide present during the reaction and to efficient by-product recovery and utilization. Efficiency is reduced by the presence of water or of alcohols. Efficiency is higher, the more concentrated the sodium hydroxide that is present.

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[138] A. F. Martin, private communication.

(c) ALKALI CELLULOSE MANUFACTURE

To prepare alkali cellulose when excess sodium hydroxide is used, the sheet cellulose is first reduced to fibrous shreds in a Stern shredder.[139] The shredded cellulose is blown into a continuous horizontal conveyor, where it is moistened by a spray of aqueous sodium hydroxide solution.[140] The resultant slurry is loaded to the ethylators without aging or ripening.

When limited sodium hydroxide is used, the alkali cellulose preparation is much more critical. The cellulose sheet is passed continuously through a bath of aqueous 50 to 76% NaOH at 55° to 130°C.[141,142] The alkali cellulose, which is swelled to maximum size after impregnation, is wiped to increase its density,[142] is aged for a few seconds at a temperature between its hardening point (15° to 18°C. below the freezing point of the aqueous sodium hydroxide used) and its degradation point (130°C.), and is cooled.[143] The aging time and temperature vary inversely with the intrinsic viscosity desired in the ethyl cellulose end product.

If the alkali cellulose is not aged, the viscosity may be controlled by the addition of air to the ethylator.[144] Viscosity may also be controlled by the use of oxygen carriers such as manganese or cobalt compounds, oxidizing agents,[145] or acid gases.[146] In essence, the intrinsic viscosity of the product is controlled by mild hydrolysis[146] or by mild oxidation[143–145] of the cellulose. If air is used as the oxidant, the amount required (shown in Table 29) is small.

The intrinsic fluidity, $[\Phi]$ (that is, the reciprocal of the intrinsic viscos-

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[139] R. L. Stern (to Hercules Powder Co.), U. S. Patent 2,028,080 (Jan. 14, 1936); *Chem. Abstracts*, **30**, 1561 (1936); A. S. Finlayson (to Hercules Powder Co.), U. S. Patent 2,313,866 (Mar. 16, 1943); *Chem. Abstracts*, **37**, 5237 (1943).

[140] "Integration of Chemical Plant Facilities," *Chem. Met. Eng.*, **52**, 129 (Sept., 1945).

[141] S. L. Bass (to The Dow Chemical Co.), U. S. Patent 2,143,855 (Jan. 7, 1939); *Chem. Abstracts*, **33**, 3150 (1939).

[142] W. R. Collings, L. DePree, and M. H. Weymouth (to The Dow Chemical Co.), U. S. Patent 2,143,863 (Jan. 17, 1939); *Chem. Abstracts*, **33**, 3150 (1939); U. S. Patent 2,145,862 (Feb. 7, 1939); *Chem. Abstracts*, **33**, 3586 (1939).

[143] F. C. Peterson and A. T. Maasberg (to The Dow Chemical Co.), U. S. Patents 2,149,309 and 2,149,310 (Mar. 7, 1939); *Chem. Abstracts*, **33**, 4421 (1939).

[144] R. B. Darling (to Hercules Powder Co.), U. S. Patent 2,492,524 (Dec. 27, 1949); *Chem. Abstracts*, **44**, 2237 (1950).

[145] E. D. Klug (to Hercules Powder Co.), U. S. Patent 2,523,377 (Sept. 26, 1950); *Chem. Abstracts*, **45**, 1344 (1951); E. D. Klug and H. M. Spurlin (to Hercules Powder Co.), U. S. Patent 2,512,338 (June 20, 1950); *Chem. Abstracts*, **44**, 8656 (1950).

[146] R. D. Freeman and M. J. Roberts (to The Dow Chemical Co.), U. S. Patents 2,159,375 and 2,159,376 (May 23, 1938); *Chem. Abstracts*, **33**, 7108 (1939); U. S. Patent 2,159,377 (July 19, 1938); *Chem. Abstracts*, **33**, 7109 (1939).

ty), has an approximately linear relationship to the weight of oxygen con-
umed. The equation of this line is

$$[\Phi] = 2.2 + 1.2x \qquad (5)$$

vhere x is the pounds of air used per 100 pounds of cellulose. The amount of air required to control viscosity varies with the aging temperature, ethyl-tion temperature, aqueous sodium hydroxide concentration, and other actors.

TABLE 29

Control of Ethyl Cellulose Intrinsic Viscosity (Darling[144])

			Air/100 lb. of cellulose	
Viscosity, cps., 5% solution[a]	Intrinsic viscosity[a]	Intrinsic fluidity	Cubic feet at standard conditions	Pounds
393	3.48	0.29	5.7	0.46
125	2.35	0.42	21.8	1.76
105	2.22	0.45	22.8	1.84
75	1.97	0.51	26.8	2.16

[a] Viscosity and intrinsic viscosity solvent: 80:20 toluene:ethanol.

(d) ETHYLATION

Ethyl cellulose is prepared by the etherification of alkali cellulose with thyl chloride. The reaction is:

$$R_{cell}(OH)_3{\cdot}3NaOH + 2\ CH_3CH_2Cl \longrightarrow R_{cell}(OH)(OCH_2CH_3)_2 + 2\ NaCl + NaOH + 2\ H_2O \qquad (6)$$

The number of moles that react varies with the degree of substitution and vith the substituent distribution. The reaction is retarded as the water oncentration increases and as the sodium hydroxide concentration de-reases.

Measurable amounts of carboxyl groups appear in the product as the esult of oxidation of the alkali cellulose or of the ethyl cellulose.

The chief by-product reactions are:

$$CH_3CH_2Cl + NaOH \longrightarrow CH_3CH_2OH + NaCl \qquad (7)$$

he rate of which is proportional to the sodium hydroxide concentration, nd

$$H_3CH_2OH + CH_3CH_2Cl + NaOH \longrightarrow CH_3CH_2OCH_2CH_3 + NaCl + H_2O \qquad (8)$$

he extent of which is proportional to the ethanol concentration and to the eaction time. This last reaction is rapid if alcohol is added[147]; otherwise it is negligible at first but increases with time as alcohol is produced by reaction 7.

Other side reactions include the oxidation of ethanol to acetaldehyde and higher aldehydes and the reaction of these aldehydes in the presence of sodium hydroxide to yield colored resinous bodies.

By-product formation and cellulose degradation are rapid if the primary ethylation rate is slow.[147]

Ethylations are carried out in jacketed, agitated, nickel-clad autoclaves. If ethyl chloride is used alone, the working pressure is about 400 lb./sq. in. gage; if a diluent is used, the pressure may be as low as 175 lb./sq. in. gage. Thorough agitation is of extreme importance. The reaction is mildly exothermic; the heat liberated is removed by condensation of the solvents on the shell.

Ethylation methods that are recognized include: single-stage with ethyl chloride alone[144,147,148]; and multistage with solid sodium hydroxide addition,[149] either with ethyl chloride alone or with ethyl chloride and a diluent. These methods may be modified by variations of time, temperature, and charge.

The alkali cellulose is prepared to conform to the ethylation conditions that are to be used. The relation of alkali cellulose composition and of ethylation conditions to efficiency at diverse degrees of substitution was studied by Swinehart and Maasberg.[149] They ethylated alkali cellulose[142] that contained from 3.2 to 4.5 moles of sodium hydroxide per glucopyranose residue and from 2.5 to 3.4 moles of water per glucopyranose residue. The alkali cellulose was reacted with a large excess of ethyl chloride at 90° to 120°C. until the D.S. was 1.7 to 2.0. At this point the reaction mass contained 1.8% residual sodium hydroxide; water formation had diluted the sodium hydroxide to a concentration of 30 to 50%.

Solid sodium hydroxide was then added to bring the sodium hydroxide concentration back up to 55 to 75%. The reaction was continued until the desired degree of substitution was obtained; water formation had again diluted the sodium hydroxide to a concentration of 30 to 50%. The minimum quantities of sodium hydroxide that are required to obtain certain degrees of substitution are shown in Table 30.

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[147] E. J. Lorand (to Hercules Powder Co.), U. S. Patent 2,096,681 (Oct. 19, 1937); *Chem. Abstracts*, **32**, 353 (1938); U. S. Patent 2,110,526 (Mar. 8, 1938); *Chem. Abstracts*, **32**, 3611 (1938); U. S. Patent 2,130,998 (Sept. 20, 1938); *Chem. Abstracts*, **32**, 9495 (1938).

[148] W. R. Collings and L. DePree (to The Dow Chemical Co.), U. S. Patent 2,163,869 (June 27, 1939); *Chem. Abstracts*, **33**, 8012 (1939).

[149] R. W. Swinehart and A. T. Maasberg (to The Dow Chemical Co.), U. S. Patent 2,254,249 (Sept. 2, 1941); *Chem. Abstracts*, **35**, 8295 (1941).

TABLE 30

Ethylation: Relation of Sodium Hydroxide:Cellulose Ratio to Degree of Substitution (Swinehart and Maasberg[149])

D.S.	Ethoxyl, %	Minimum NaOH:cellulose ratio Weight	Minimum NaOH:cellulose ratio Moles	Minimum NaOH concentration, %
2.2	44	1.1	4.5	48
2.3	46	1.4	5.7	50
2.5	48.5–49	1.7	6.9	56
2.6	50	2.0	8.1	60
2.8	52	2.5	10.1	74

When ethyl chloride is used alone, a multistage reaction with sodium hydroxide addition is more efficient than a single-stage reaction; a multistage reaction containing such a diluent as benzene is even more efficient. The relation of these factors to efficiency is shown in Table 31.

TABLE 31

Ethylation: Relation of Method to Efficiency (Swinehart and Maasberg[149])

		Ethyl chloride:cellulose weight ratio consumed			Efficiency, %[a]		
D.S.	Ethoxyl, %	One-stage NaOH	Two-stage NaOH	Two-stage NaOH in benzene	One-stage NaOH	Two-stage NaOH	Two-stage NaOH in benzene
0.6	15	1.1	0.8	0.45	22	30	53
1.3	30	1.5	1.1	0.9	38	51	62
1.6	35	2.4	1.2	1.1	28	57	62
1.9	40	2.5	1.5	1.35	33	54	60
2.25	45	2.6	2.2	1.6	36	43	58
2.42	47.5	2.9	2.6	1.9	35	39	53
2.47	48	3.1	2.7	2.0	33	38	51
2.62	50	—	—	3.17	—	33	—

[a] First-stage efficiency 50 to 60%.

In practice, more than the minimum quantity of sodium hydroxide shown in Table 31 is used. Since water retards reaction 6, the strength of the sodium hydroxide that is used to prepare the alkali cellulose must be increased as the desired degree of substitution increases. The minimum concentration required is shown in the last column of Table 30.

The consumption of ethyl chloride during the reaction can be followed by analysis of the reaction mass for salt and sodium hydroxide. When the desired ethyl chloride consumption is reached, the sample is tested for approval with respect to degree of substitution and viscosity.

(e) PRECIPITATION

The ethyl cellulose formed amounts to about 8% of the reaction mass; it must be separated from the mixture of salt, sodium hydroxide, water, and solvents in which it is dissolved.

The reaction mass, if viscous, is diluted,[150] strained, and precipitated[150,151] either in an autoclave or in separate equipment. When the volatile solvents (ethyl chloride, ether, ethanol, and benzene) are flashed off, the ethyl cellulose is left in suspension as dense, porous granules. If excess sodium hydroxide was used, the excess is recovered. The solvents are condensed, fractionated, and re-used. Excess ethanol and ether are either sold or reconverted to ethyl chloride.

(f) BY-PRODUCT CONVERSION

Effective by-product recovery and conversion is the key to efficient operation. Ethanol and ethyl ether are reconverted to ethyl chloride by high-temperature, aqueous-phase hydrochlorination with hydrogen chloride in the presence of a heavy metal salt catalyst such as zinc chloride.[152,153] Ethyl ether is also reconverted to ethyl chloride by high-temperature, gas-phase hydrochlorination over a solid catalyst.

(g) PURIFICATION

The impure ethyl cellulose is washed with water until free of alkali and salt. The washing is carried out in one or more agitated wash tanks; the filter media may be false bottoms in the tanks or they may be separate filter units. If the granules are coarse they may be ground through a knife mill to increase their leachability.

The ethyl cellulose is given special purification treatments during washing to prepare it for its intended end use. Such treatments may include bleaching with sodium hypochlorite[154] or with sodium chlorite, acid treatment,[155] deashing,[156] or fractionation.[157,158] Following purification, the ethyl cellulose is centrifuged and dried to a low moisture content.

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[150] W. R. Collings (to The Dow Chemical Co.), U. S. Patents 2,121,731 and 2,121,732 (June 21, 1938); *Chem. Abstracts*, **32**, 6461 (1938).

[151] H. M. Spurlin (one-half to Hercules Powder Co., one-half to The Dow Chemical Co.), U. S. Patent 2,249,673 (July 15, 1941); *Chem. Abstracts*, **35**, 6791 (1941).

[152] H. M. Spurlin (to Hercules Powder Co.), U. S. Patent 2,084,710 (June 22, 1937); *Chem. Abstracts*, **31**, 5816 (1937).

[153] R. P. Carter (to Hercules Powder Co.), U. S. Patent 2,396,639 (Mar. 19, 1946); *Chem. Abstracts*, **40**, 4076 (1946).

(h) STABILITY OF ETHYL CELLULOSE

Ethyl cellulose is stable toward such chemical agents as alkalies, salts, and water. It is stable in the presence of sunlight or ultraviolet light and at temperatures above its softening point, provided that it has been properly prepared and formulated.

The thermal stability of ethyl cellulose is related to the presence of functional groups, such as carbonyl and carboxyl. When the purification of the ethyl cellulose is completed, the carboxyl groups that were formed by oxidative ring or chain breakage may be left in any degree of neutralization from a form in which they are completely bound by base metals to a metal-free form. In the final formulation there must be a suitable balance of acidity to basicity. If the formulation is too acidic, it will degrade in viscosity and strength; if the formulation is too basic, it will discolor when subjected to heat. This effect is of minor concern in uses that do not involve heat, although Evans and Spurlin[156] found that bound metal increases the viscosity of solutions in nonpolar solvents over that which is found for deashed ethyl cellulose.

The oxidation of ethyl cellulose was studied by Evans and McBurney[159,160] who passed oxygen through ethyl cellulose of 0.9 intrinsic viscosity at 50° to 109°C. with and without irradiation by ultraviolet light. Their mechanism for the oxidation is based upon hydroperoxide and acetaldehyde formation. Their work showed the sensitizing action of easily oxidized material, such as acetaldehyde and oxidized ethyl cellulose itself, and the effectiveness of such oxidation retardants and inhibitors as diamylphenol,[137] diphenylamine,[159] and copper salts.[161] Chamberlain[19] in further work found

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[154] J. McHard and F. C. Peterson (to The Dow Chemical Co.), U. S. Patent 2,238,912 (Apr. 22, 1941); *Chem. Abstracts*, **35**, 4951 (1941).

[155] A. S. Finlayson (to Hercules Powder Co.), U. S. Patent 2,178,630 (Nov. 27, 1939); *Chem. Abstracts*, **34**, 1482 (1940).

[156] E. F. Evans and H. M. Spurlin, *J. Am. Chem. Soc.*, **72**, 4750 (1950).

[157] H. M. Spurlin (to Hercules Powder Co.), U. S. Patent 2,214,070 (Sept. 10, 1940); *Chem. Abstracts*, **35**, 893 (1941).

[158] J. H. Sharphouse, P. R. Hawtin, John Downing, and W. H. Groombridge (to British Celanese, Ltd.), Brit. Patent 556,664 (Oct. 15, 1943); *Chem. Abstracts*, **39**, 1992 (1945). See I. Okamura, *Cellulosechemie*, **14**, 135 (1933).

[159] L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1256 (1949).

[160] E. F. Evans and L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1256 (1949).

[161] P. VanWyck (to Hercules Powder Co.), U. S. Patents 2,561,892 and 2,561,893 (July 24, 1951).

that their mechanism is well supported, but that the rate of oxidation depends largely upon the history of the sample.

The heat stability of ethyl cellulose is determined in practice under the conditions of its end use. Base flake formulated into molding powder for plastic end uses is tested by retention at 240°C. in the tunnel of an injection-molding press or a compression-molding press for an extended time. The change in intrinsic fluidity is then determined. Chamberlain[19] found that the exclusion of oxygen from the press by nitrogen blanketing does not bring about great changes in viscosity, but does definitely improve color. Since there is not sufficient oxygen in a press to produce great changes in viscosity, it is found that the change in fluidity varies with the history of the sample, and that both hydrolysis and oxidation may occur.

When properly prepared and formulated, ethyl cellulose will produce low-color plastics with high retention of strength and durability over a broad range of temperature.

Ethyl cellulose for outdoor uses is tested by atmospheric exposures in a suitable climate. Ethyl cellulose having a small intrinsic fluidity rise is most suitable for these uses, and the working range below excessive fluidity improves at higher viscosities.

(i) ETHYL CELLULOSE PLASTIC

Ethyl cellulose plastic articles may be fabricated by extrusion or by injection molding. The properties of the plastic may be varied to yield hard-surfaced extruded shapes, medium-hard molded shapes, or molded shapes having outstanding low-temperature flexibility. Table 32 summarizes the properties of ethyl cellulose plastics.[19] The values given are conservative, but they exceed the proposed ASTM specifications for ethyl cellulose molding compounds.

(j) ETHYL CELLULOSE SHEETING

Ethyl cellulose sheeting contains little plasticizer; its properties are essentially those of the base flake. Table 33 (see p. 924) shows the properties of ethyl cellulose sheeting.[19]

(k) ETHYL CELLULOSE BASE FLAKE

The solubility and the thermoplasticity of ethyl cellulose depend upon its degree of substitution and upon its intrinsic viscosity. The softening temperature and the melting temperature decrease with increasing degree of substitution to a minimum at D.S. 2.50; above this substitution these properties again increase. At a fixed degree of substitution, the softening

TABLE 32. Average Properties of Ethyl Cellulose Plastics (The Dow Chemical Company[19])

Property	Test method A.S.T.M.	Extrusion hard	Injection	
			Medium	Low temperature
Mechanical properties:				
Tensile strength, 77°F., lb./sq. in.	D638-49T	7000	5000	3500
Elongation in tension, 77°F., %	D638-49T	6	10–30	10–25
Modulus of elasticity in tension, 77°F., lb./sq. in.	D638-49T	3×10^5	2×10^5	1.5×10^5
Impact strength, Izod, notched,				
77°F., ft.-lb./in.	D256-47T	2.0	2.5	4.5
0°F., ft.-lb./in.		1.5	1.0	2.0
−40°F., ft.-lb./in.		1.0	0.5	1.2
Hardness, Rockwell	D785-48T	R110	R100	R70
Thermal properties:				
Flow temperature, °C.	D569-48	155	145	150
Heat distortion, °C., 264 lb./sq. in.	D648-45T	70	60	55
Weight loss on heating, max., %	D787-46T	0.2	0.4	2.0
Electrical properties:				
Dielectric constant				
10^3 cycles/sec.	D150-47T	3.3	3.1	3.4
10^6 cycles/sec.		3.2	3.0	3.2
10^8 cycles/sec.		3.0	2.8	2.9
Power factor, %				
10^3 cycles/sec.	D150-47T	0.3	1.3	1.0
10^6 cycles/sec.		2.0	1.6	2.4
Chemical properties:				
Chemical resistance	—	[a]	[a]	[a]
Water sorption, % gain in 24 hrs.	D570-42	1.5	1.2	1.5
Water solubility, max., %	D570-42	0.2	0.2	0.4
Fabrication:				
Specific gravity	D792-48T	1.12	1.10	1.10
Injection molding, flow grade		H	M	MH
Machine temperature, °F.		—	430	420
Machine pressure, lb./sq. in. gage		—	15,000	15,000
Extrusion temperature, °F.		440	410	410
Color possibilities		Opaque	Transparent to opaque	
Machining properties		Excellent	Good	Good

[a] Chemical resistance: weak acids, no effect; strong acids, severe attack; weak alka- s, no effect; strong alkalies, slight attack; organic solvents, widely soluble.

TABLE 33. Average Properties of Ethyl Cellulose Sheeting (The Dow Chemical Company[19])

Property	Test method A.S.T.M.	Value	Thickness, in.
1. Mechanical properties:			
Tensile strength, lb./sq. in.	—	8000	—
Elongation, %	—	20–35	—
Folding endurance, M.I.T. double folds, 75°F., 50% R.H.	—	2750	0.001
Bursting strength, lb./sq. in.	—	85	0.001
Tear strength, Elmendorf, g./0.001 in.	—	97	0.005
2. Thermal properties:			
Softening temperature, °C.	—	154	—
Melting temperature, °C.	—	191	—
Specific heat, B.t.u./lb.	—	0.348	—
3. Electrical properties:			
Dielectric constant			
60 cycles/sec.	D150-44T	3.2	—
10^3 cycles/sec.	—	3.1	—
10^6 cycles/sec.	—	3.0	—
Power factor, %			
60 cycles/sec.	D150-44T	1.2	—
10^3 cycles/sec.	—	0.4	—
10^6 cycles/sec.	—	2.0	—
Dielectric strength, volts/0.001 in.	—	3500	0.002
4. Chemical properties:			
Water sorption, %, 100°F., 100% R.H.	—	3.3	—
%, 24-hr. immersion, 80° F.	D570-42	7.5	—
Normal moisture content, %, 75°F., 50% R.H.	—	1.4–1.7	—
Moisture vapor transmission, g./100 sq. in./24 hrs., 100°F., 95% R.H.	Modified General Foods[b]	35	0.002
Chemical resistance	—	[a]	—
5. Fabrication:			
Specific gravity	D71-27	1.15	—
6. Optical properties:			
Refractive index, n_D^{20}	—	1.47	—
Transmission of white light, %	—	88–92	—
Ultraviolet cut-off, A.	—	2200	—
Transmission of infrared (except narrow absorption band at 10^{-3} cm.), %	—	90	—
Fade-Ometer, 200 hrs.			
yellowing		almost none	
embrittlement		none	

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[a] Chemical resistance: weak acids, no effect; strong acids, severe attack; weak alkalies, no effect; strong alkalies, slight attack; organic solvents, widely soluble.

[b] Thwing-Albert Vapometer in modified General Foods Cabinet; cabinet and procedure modified by The Dow Chemical Co.[19]

and melting temperature increase as the intrinsic viscosity increases. The relation among these factors is shown in Figure 62; the fine lines represent the spread in temperature due to variant intrinsic viscosity.[162]

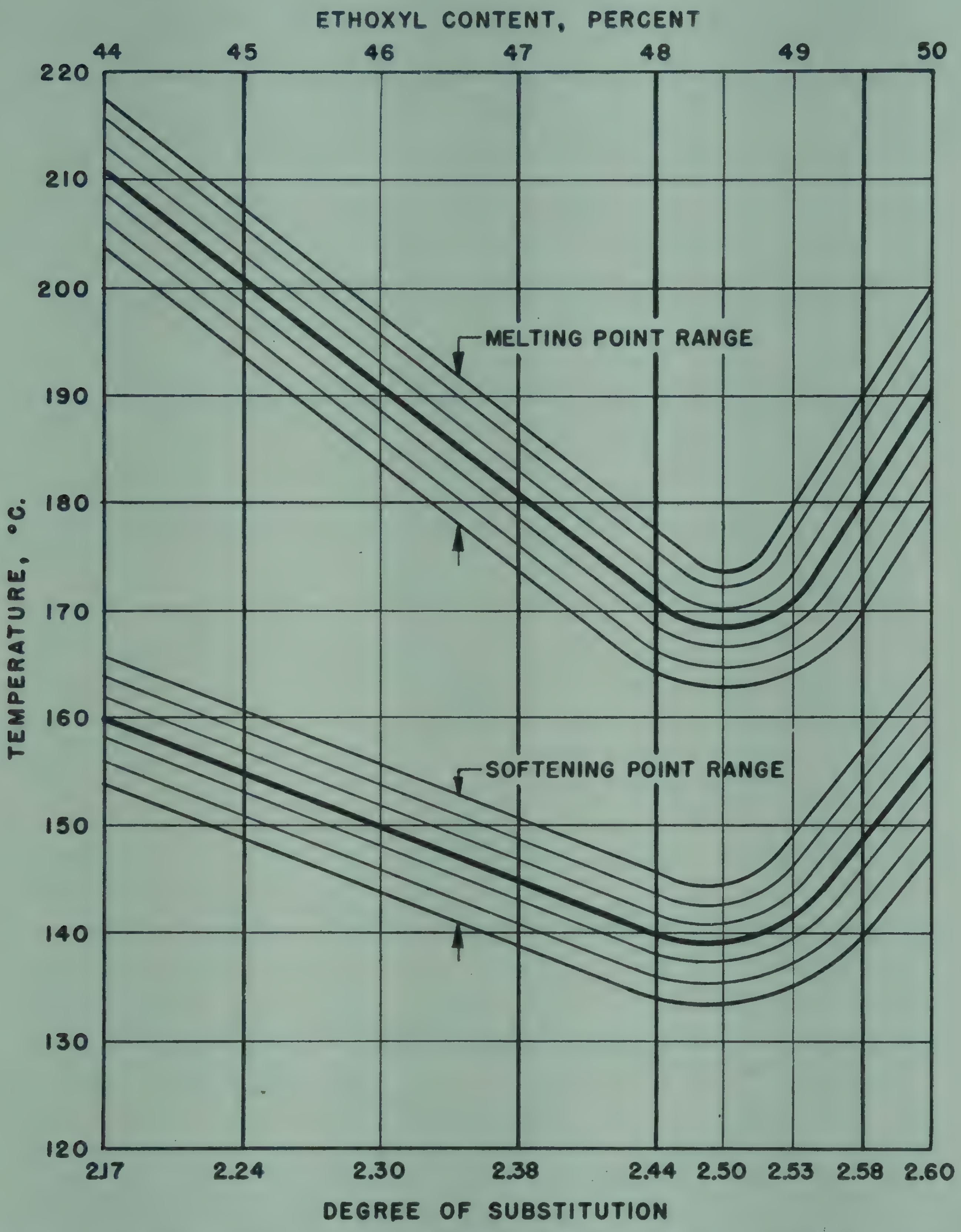

Fig. 62. Ethyl cellulose: relation of softening–melting point range to degree of substitution and to intrinsic viscosity (The Dow Chemical Co.[19]).

The solubility of ethyl cellulose varies in the same manner as its thermoplasticity; ethyl cellulose of D.S. 2.1 to 2.4 is soluble only in 70:30 benzene:methanol, in 60:40 toluene:ethanol, in methyl acetate, or in ethylene dichloride. When the substitution is increased above D.S. 2.4, solubility in a wide variety of solvents results. Above D.S. 2.55 alcohol solubility is lost but hydrocarbon dispersibility is retained.[137,162] If the substitution is fixed, the solubility increases as the viscosity is lowered.

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[162] *Ethocel Handbook,* The Dow Chemical Co., Midland, Mich., 1940.

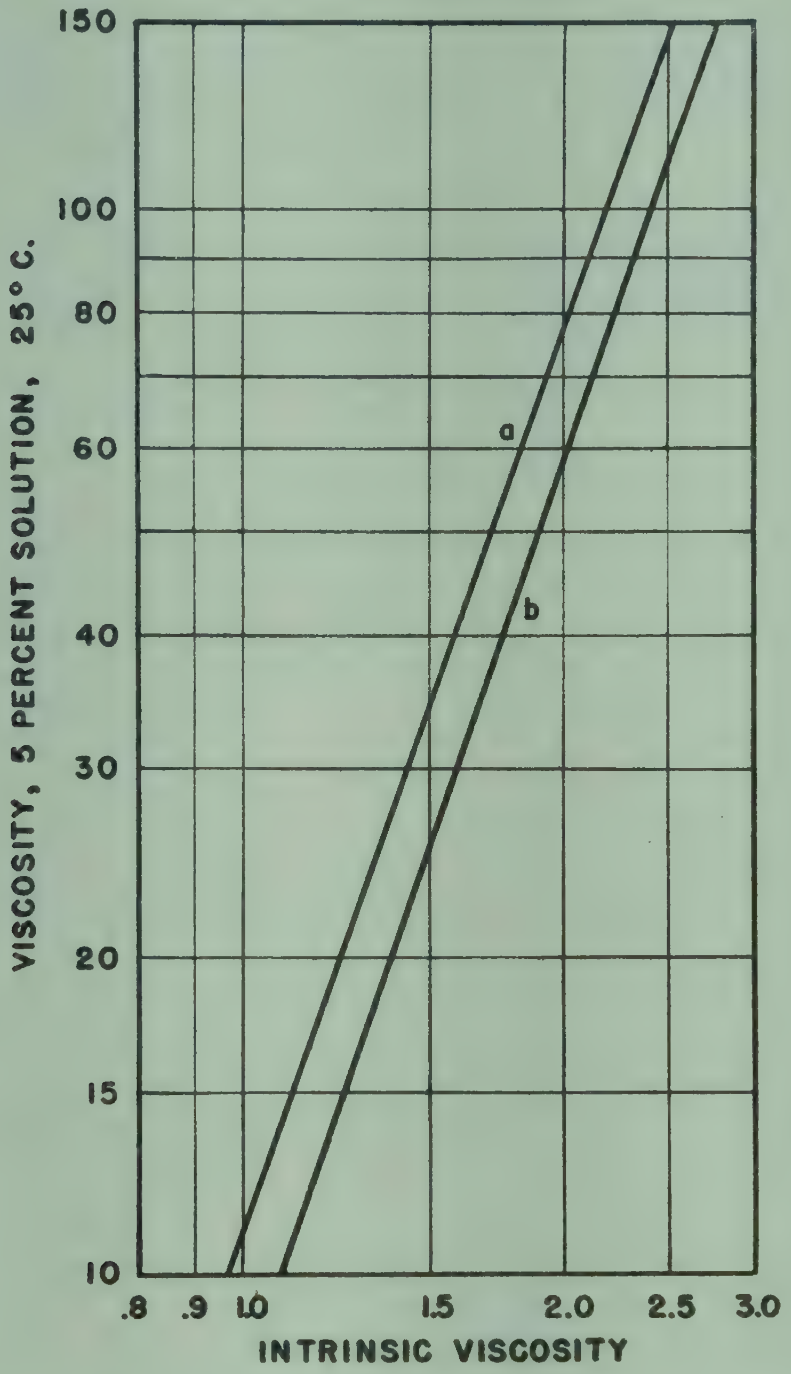

Fig. 63. Ethyl cellulose: relation of viscosity of 5% solution (in cps.) at 25°C. to intrinsic viscosity (The Dow Chemical Co.[19]). Lines: *a*, D.S. 2.5 in 80:20 toluene:ethanol; *b*, D.S. 2.3 in 70:30 benzene:methanol.

Two substitution grades of ethyl cellulose satisfy most needs. D.S. 2.24 to D.S. 2.38 (45.0 to 47.0% ethoxyl) is used for plastics and wherever hardness, strength, and heat resistance are factors; D.S. 2.44 to D.S. 2.58 (48.0 to 49.5% ethoxyl) is used where ready solubility, wide compatibility, and ready softening are factors. Each substitution grade is produced in several iscosity types. A low-viscosity type is used when high concentration in olution or high flow is a factor; a high-viscosity type is used when strength, lexibility, or hardness is a factor.

The intrinsic viscosity has been used in this Section of Chapter IX so hat different cellulose ethers may be compared directly. Commerical ethyl ellulose, however, is sold on the basis of the viscosity of its 5% solution by veight in a specific solvent. The specific solvents for 5% solution viscosity neasurements are:

Degree of substitution	Ethoxyl, %	Solvent composition by volume
2.24–2.38	45.0–47.0	70:30 benzene:methanol
2.44–2.58	48.0–49.5	80:20 toluene:ethanol

Certain specifications require that the viscosity of D.S. 2.24 to 2.38 ethyl ellulose be reported in terms of 60:40 toluene:ethanol solvents; the ratio f the viscosity in 60:40 toluene:ethanol to the 70:30 viscosity is 1.34:1.

The intrinsic viscosity of ethyl cellulose in a specific solvent is related to ts 5% viscosity in the same solvent by the empirical equation[19]:

$$(5\% \text{ solution viscosity, cps.}) = A\ (\text{intrinsic viscosity})^{2.9} \qquad (9)$$

vhere the intercept constant, A, is:

A	D.S.	Solvent
(a) 10.6	2.5	80:20 toluene: ethanol
(b) 7.2	2.3	70:30 benzene:methanol

igure 63 shows the relation of 5% solution viscosity to intrinsic viscosity or commercial ethyl cellulose.

The viscosity of ethyl cellulose solutions of finite concentration is lower n good solvents than in poorer solvents. The viscosity is influenced by the ase-exchange state of the end groups.[156] When concentrations of 5% or igher are used, the relation of viscosity to concentration may be expressed y Philippoff's equation[163]:

$$\eta_r = (1 + [\eta]C/8)^8 \qquad (10)$$

Kauppi and Bass[164] used equation (10) to construct a viscosity-concenration chart (Fig. 64) for ethyl cellulose at finite concentrations. If the iscosity of an ethyl cellulose is known at one concentration, its viscosity at ny other concentration may be found from Figure 64. Philippoff found hat any means of altering the viscosity (for example, by changing solute, solvent, or temperature) changed the intercepts of a line but not its linearity.

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[163] W. Philippoff and K. Hess, *Z. physik. Chem.*, **31B**, 237 (1936).

[164] T. A. Kauppi and S. L. Bass, *Ind. Eng. Chem.*, **29**, 800 (1937).

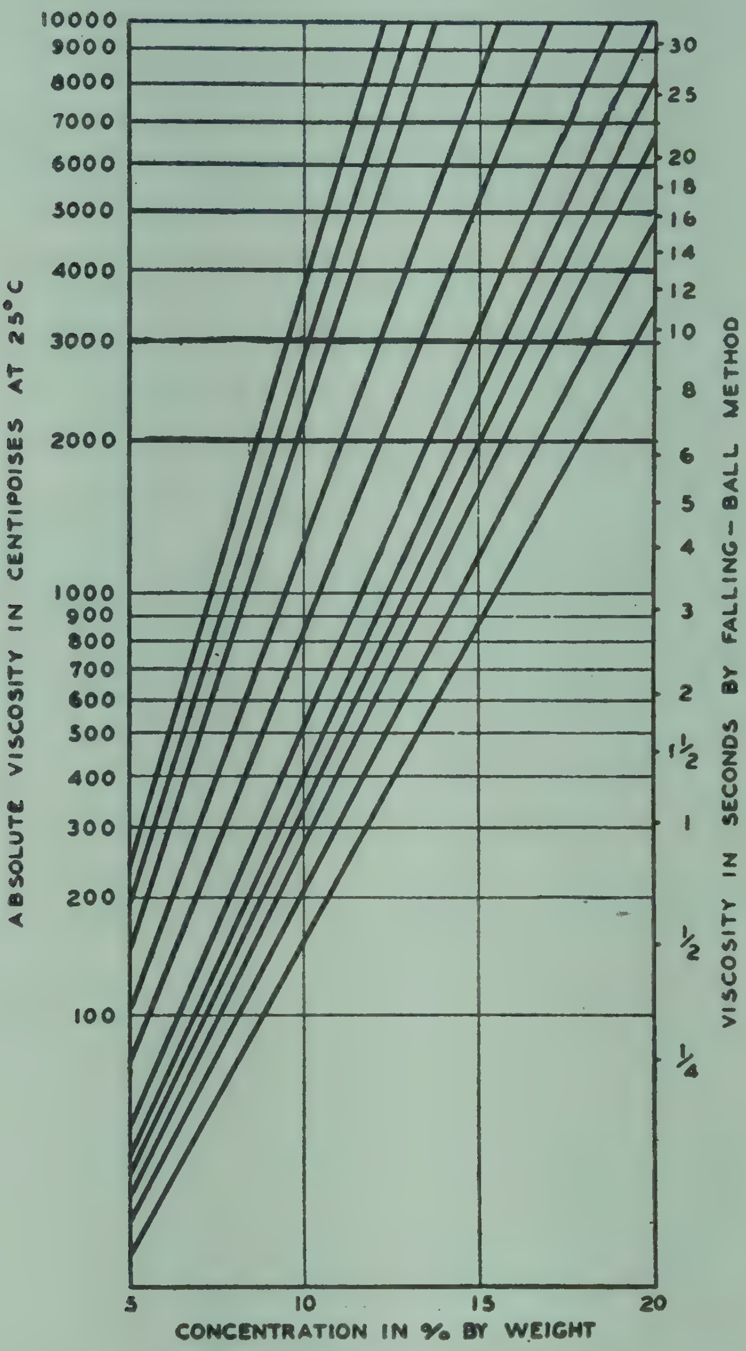

Fig. 64. Ethyl cellulose: viscosity–concentration chart (Kauppi and Bass[164]).

(l) FORMULATION OF ETHYL CELLULOSE

The formulation of ethyl cellulose is discussed by the manufacturers.[137,162] Aromatic hydrocarbon–alcohol blends are suitable solvents, with modification, for most purposes. Plasticizers, usually ethers, esters, or nonsolvent oils, impart flexibility and flow. Resins impart hardness and adhesion. Ethyl cellulose is compatible with many resins and with nitrocellulose, but not with most other high polymers. Ethyl cellulose is compatible with many waxes to form melts; compatibility is increased by the use of mutually compatible materials.

(m) HIGH-ETHOXYL ETHYL CELLULOSE

Nearly completely substituted ethyl cellulose of D.S. 2.60 to 2.80 (ethoxyl ontent 50.0 to 52.5%) has been prepared by the method of Swinehart and Iaasberg.[149] The large amounts of sodium hydroxide and salt involved end to separate the reaction mass into layers, so that decreased diffusion engthens the reaction time. The quantities of reagents involved are shown n Tables 30 and 31.

Ethyl cellulose of D.S. 2.6 to 2.8 is dispersed in hydrocarbons. Plasticizaion is required to increase strength and to eliminate haze. No plasticizer as been found to act as a solvent or to lower the melting point. High-thoxyl ethyl cellulose is incompatible with ethyl cellulose of lower substituion. Sheeting of high-ethoxyl ethyl cellulose has a tensile strength of 5000 b./sq. in., an elongation of 10 to 30%, a melting point of 240°C., and no oftening point.

(n) LOW-SUBSTITUTED ETHYL CELLULOSE

The very low-substituted ethyl celluloses resemble the more common vater- or alkali-soluble methyl celluloses, carboxymethyl celluloses, and ydroxyalkyl celluloses in properties. Ethyl cellulose of D.S. 0.3 to 0.5 is oluble only in 4 to 10% aqueous sodium hydroxide.[84,125] Ethyl cellulose f D.S. 0.7 to 1.3 is soluble in cold water.[19,84,125] Such ethers are soluble at till lower substitution values when the solutions are chilled or when the ellulose has been degraded.

Alkali-soluble ethyl cellulose is prepared by the treatment of alkali celluose with ethyl sulfate[123,124] or with ethyl chloride.[19,126] The residual soium hydroxide is neutralized, and the product is washed free of salt, and hen dried. The alkali-soluble ethers are dissolved in 4 to 10% aqueous JaOH, cast or formed, and coagulated by acid treatment. The washed nd dried sheeting resembles cellophane.

Water-soluble ethyl cellulose is produced by the ethylation of alkali cellose with ethyl chloride.[19] The alkali cellulose composition and the reacon temperature are controlled to yield the type of solubility and the gelaon temperature desired.

(o) MODIFIED ETHYL CELLULOSE

Sönnerskog[165] and Jullander[166] have described ethyl hydroxyethyl celluses. At M.S. 0.9 hydroxyethoxyl and D.S. 0.9 ethoxyl, the product is water-soluble, whereas at M.S. 0.7 and D.S. 1.34 the product is soluble in methylene chloride–alcohol.

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[165] S. Sönnerskog, *Svensk Papperstidn.*, 48, 413 (1945).
[166] I. Jullander, *Svensk Papperstidn.*, 55, 197 (1952).

5. Methyl Cellulose

The uses of methyl cellulose stem from its cold-water solubility and from the toughness of its sheeting. Methyl cellulose thickens water solutions without precipitation over a pH range from 3 to 12. Methyl cellulose gels from solution upon heating or upon salt addition; this feature is utilized in many applications. Methyl cellulose can be cross-linked to insolubility after forming. The strength and toughness of methyl cellulose films add strength to adhesives in which methyl cellulose is compounded. The surface-active properties of methyl cellulose aid in the stabilization of latexes and emulsions. The physiological inertness and the storage stability of methyl cellulose permit its use in cosmetics, pharmaceuticals, and food products.

Unplasticized methyl cellulose is heat resistant and not thermoplastic; when methyl cellulose is plasticized by certain liquids that dissolve it at high temperatures, the product is thermoplastic.[167]

Methyl cellulose is made in several ranges of substitution. Commercial methyl cellulose (D.S. 1.6 to 2.0, methoxyl content 26.5 to 32.6%) is soluble in cold water; nearly completely substituted methyl cellulose (D.S. 2.4 to 2.8, methoxyl content 38.0 to 43.0%) is soluble in polar organic solvents; low-substituted methyl cellulose (D.S. 0.1 to 0.9, methoxyl content 2 to 16%) is soluble in 4 to 10% aqueous sodium hydroxide.

Chemically modified methyl celluloses combine the properties of methyl cellulose with those of other cellulose ethers.

Methyl cellulose is prepared by the etherification of alkali cellulose with methyl chloride, followed by the isolation, washing, and drying of the product.

(a) RAW MATERIALS

Methyl cellulose is prepared from wood or cotton cellulose suitable for ethylation. Very high viscosity grades are made from pulp having a 0.5% viscosity of 40 to 60 cps. (viscosity in 0.5% cupriethylenediamine solution, TAPPI Standard T 230). Refrigeration-grade methyl chloride and sodium hydroxide suitable for ethylation are used.

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[167] G. K. Greminger, R. M. Upright, and L. H. Silvernail, in *Protein and Synthetic Adhesives*, Chapter VII, *Tappi Monograph Series No. 9*, Technical Association of the Pulp and Paper Industry, New York, N. Y. (1952); L. H. Silvernail (to The Dow Chemical Co.), U. S. Patent 2,602,755 (July 8, 1952); Chem. Abstracts, **46**, 9891 (1952).

(b) METHYLATION

Methyl cellulose is prepared from alkali cellulose that contains limited odium hydroxide.[141–143] The aging time varies from a few seconds to a umber of minutes. The time and temperature chosen vary inversely as he viscosity desired. The reactions are similar to equations 6, 7, and 8.

Methylations are carried out in jacketed, agitated, nickel-clad autolaves at a working pressure of about 200 lb./sq. in. gage. The reaction is ildly exothermic; the heat liberated is removed by condensation of the olvents on the shell.

The relation of alkali cellulose composition to methyl cellulose properties as studied by Maasberg and others.[168] An alkali cellulose prepared from 7.8 to 57.2% NaOH and containing a weight ratio of sodium hydroxide to ellulose of 0.9 to 1.2 and a weight ratio of water to cellulose of 0.9 to 1.5 ielded, on methylation with a slight stoichiometrical excess of methyl hloride at 50° to 100°C., a cold-water-soluble methyl cellulose of D.S. 1.6 o 2.0 that could be washed with hot water at 85° to 100°C. and dried. he physical properties of the product were controlled by the relation of ime to temperature and pressure during processing.[169]

Methylation efficiency varies from 70 to 80% for alkali-soluble methyl ellulose to 40 to 50% for water-soluble methyl cellulose.

(c) METHYL CELLULOSE BASE FLAKE

Methyl cellulose base flake[170] is a white powder of bulk density 0.3 to 0.5 ./ml. It is heat stable up to 225°C., but it browns slightly upon continued eating above 190°C., and chars without softening at 225° to 230°C. It s soluble in cold water, but insoluble in hot water or in saturated salt soluions.

(d) METHYL CELLULOSE SOLUTIONS

Methyl cellulose solutions are prepared by wetting the powdery base flake ith water at 75° to 80°C., and then adding the remaining water while ooling and agitating. Solution clarity is improved by chilling to below 0°C.

Figure 65 shows the relation of solution viscosity to concentration for ethyl celluloses having intrinsic viscosities (in water at 20°C.) of from

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[168] A. T. Maasberg (to The Dow Chemical Co.), U. S. Patent 2,160,782 (May 30, 939); *Chem. Abstracts*, **33**, 7563 (1939).

[169] R. W. Swinehart and A. T. Maasberg (to The Dow Chemical Co.), U. S. Patents 331,864 and 2,331,865 (May 12, 1943); *Chem. Abstracts*, **38**, 1693 (1944).

[170] *Methocel*, The Dow Chemical Co., Midland, Mich., 1949.

1.4 to 7.3. The nominal 2% solution viscosities are shown in parentheses.

The intrinsic viscosity of methyl cellulose in water is related to its 2% viscosity in water at 20°C. by the empirical equation[19]:

$$(2\% \text{ viscosity, cps.}) = A(\text{intrinsic viscosity})^{3.6} \tag{11}$$

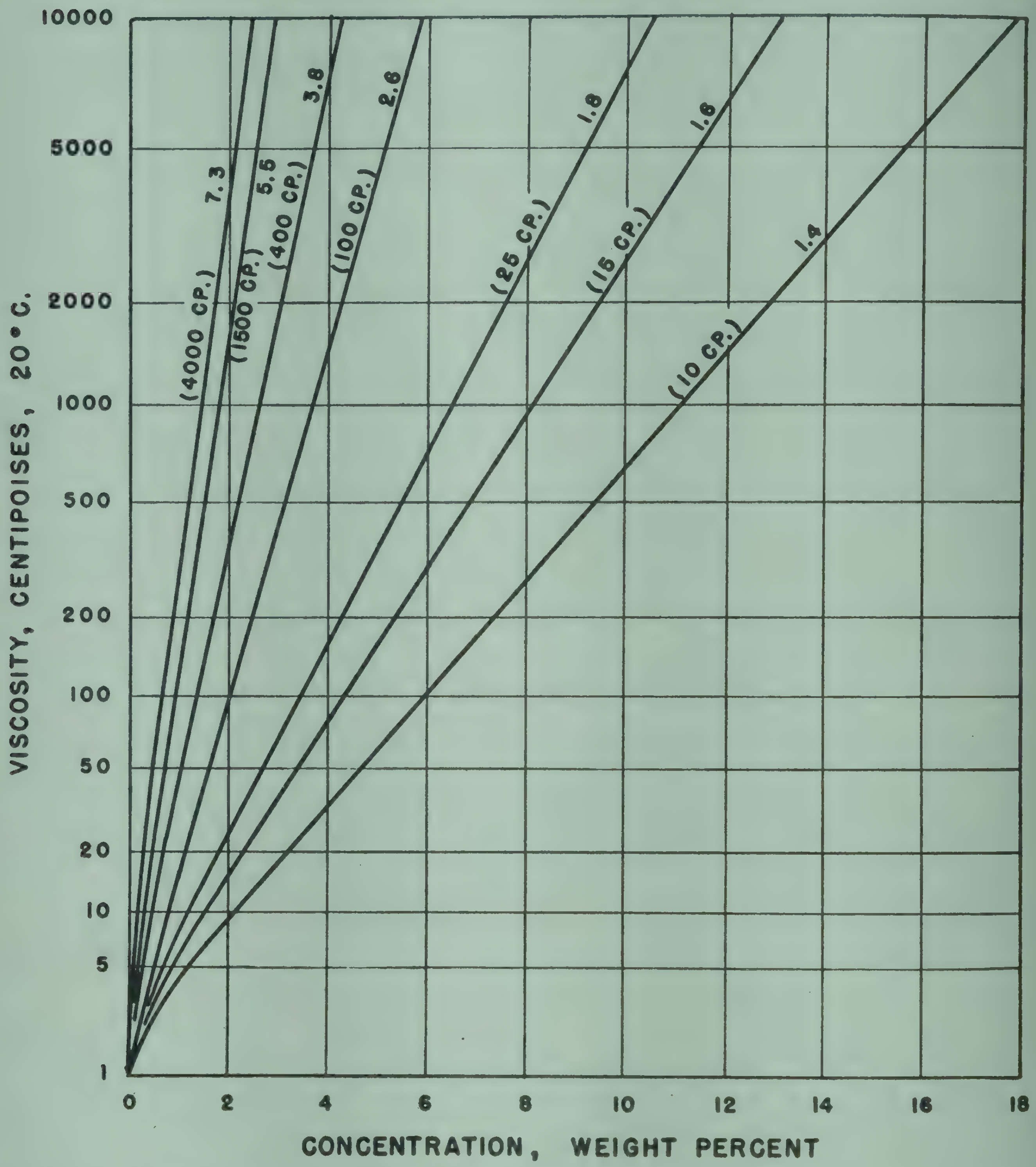

Fig. 65. Methyl cellulose: viscosity–concentration chart (The Dow Chemical Co.[19]). Values of intrinsic viscosity and of viscosity in 2% solution in water at 20°C. are shown on the curves.

where the intercept constant, A, is 0.34 for granular methyl cellulose and 0.71 for fibrous methyl cellulose. The difference in intercepts between types is due to the processing of the granular form.[169] Figure 66 shows the

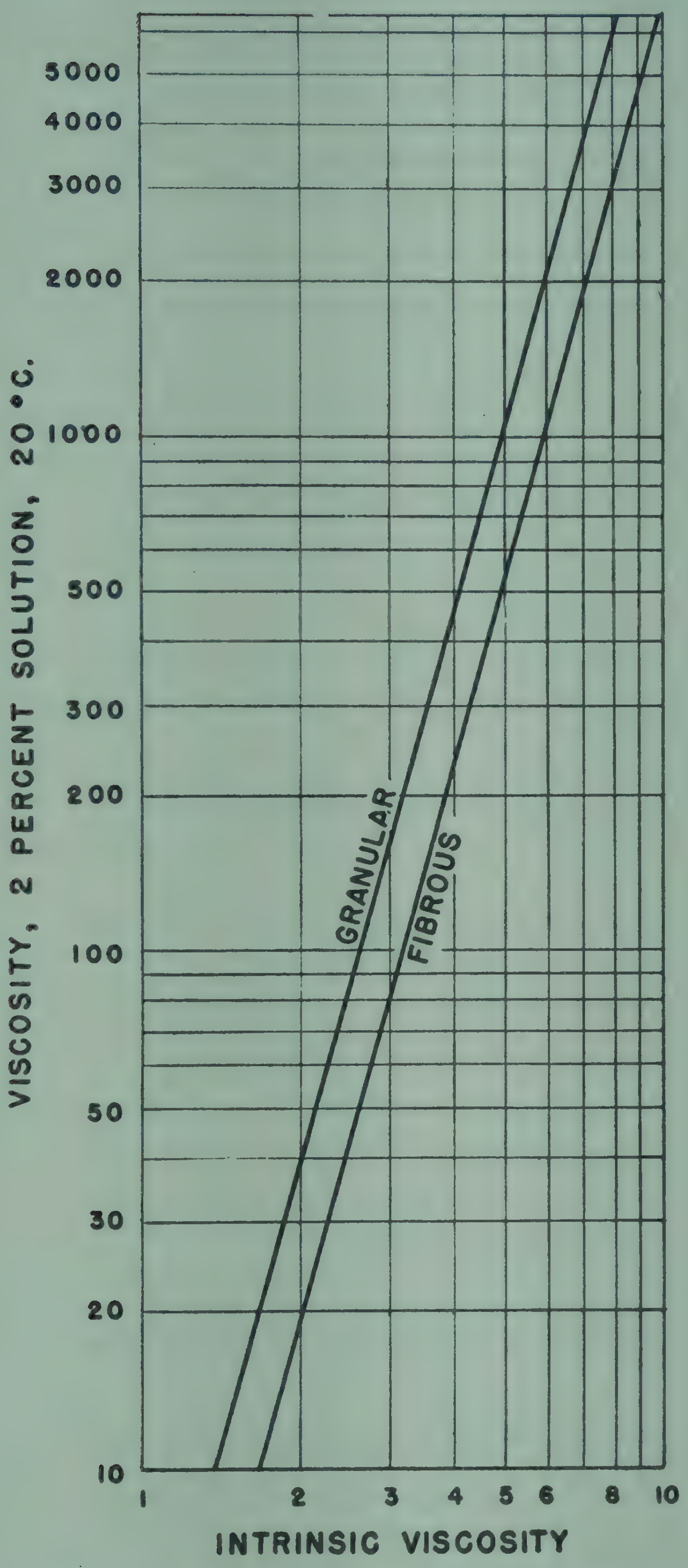

Fig. 66. Methyl cellulose: relation of viscosity of 2% water solution at 20°C. to intrinsic viscosity (The Dow Chemical Co.[19]).

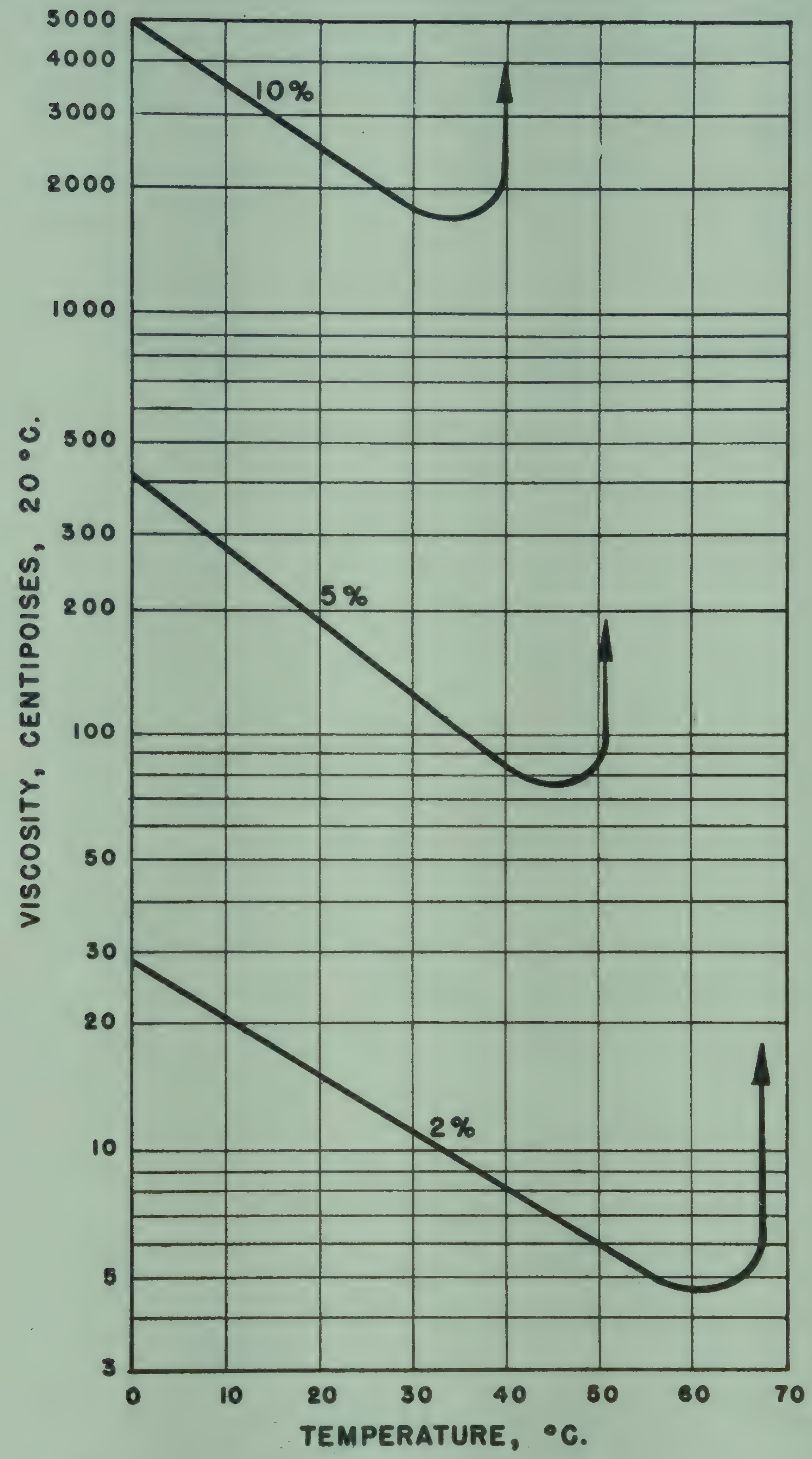

Fig. 67. Methyl cellulose: relation of solution viscosity and gel point to temperature and concentration (The Dow Chemical Co.[19]). (Intrinsic viscosity, 2.0.)

relation of 2% solution viscosity at 20°C. to intrinsic viscosity for commercial methyl celluloses.

When a methyl cellulose solution is heated, the viscosity decreases to a minimum just below the gelation temperature, then rises rapidly when the gel point is reached. The relation of solution viscosity to temperature is shown in Figure 67 for methyl cellulose of intrinsic viscosity 2.0. The gelation temperature decreased as the concentration increased.

The effect of salts[167] is similar to that of heating. The effect of sodium chloride addition to a 2% solution of methyl cellulose of intrinsic viscosity 5.5 is:

Salt concentration, %	Gelation temperature, °C.
0	50
1	50
5	44
10	33

Solution of methyl cellulose in water reduces the surface tension of the liquid–air interface from 72 dynes/cm. for water alone to a value of 50 dynes/cm. The surface tension is independent of viscosity and concentration.

(e) METHYL CELLULOSE SHEETING

Methyl cellulose sheeting has been cast from water solutions. Such sheeting can be plasticized by moisture. The properties of methyl cellulose sheeting are shown in Table 34. The flexibility of methyl cellulose sheeting

TABLE 34

Properties of Methyl Cellulose Sheeting (The Dow Chemical Company[170]) at 73°F. and 50% Relative Humidity

Property	Value
Specific gravity	1.37–1.45
Tensile strength, lb./sq. in.	8500–11,400
Elongation, %	10–15
M.I.T. double folds	12,000
Ultraviolet	
Resistance	Excellent
Transmission, 0.001-in. film, 400 mμ, %	90
290 mμ, %	84
210 mμ, %	54
Oil resistance (vegetable, animal, and mineral oils)	Impervious
Water content, %	6.5

is increased by plasticization. Plasticizers and additives include water, sugars, glycols, polyglycols, phosphates, alcohol amines, and hygroscopic salts.

(f) COMPATIBILITY

Methyl cellulose can be blended with starches, glues, soaps, dextrins, and water-dispersible natural gums. Methyl cellulose is compatible with many water-soluble resins and up to 40% with starches.

(g) INCREASING WATER RESISTANCE

Methyl cellulose can be made insoluble by chemical cross-linking of its unetherified hydroxyls by bifunctional compounds. Agents that are used include citric acid, glyoxal,[171] dimethylolurea, water-soluble melamine–formaldehyde resins, quaternary ammonium salts, and water-soluble urea–formaldehyde resins.

(h) HIGH-METHOXYL METHYL CELLULOSE

Nearly completely substituted methyl cellulose (D.S. 2.4 to 2.8) is soluble in polar organic solvents and in alcohol–aromatic hydrocarbon mixtures. This ether may be prepared by the ethyl cellulose process[141–144,148,149] or by modification of the method of Maasberg.[168] This ether may be used to thicken organic solutions.

(i) ALKALI-SOLUBLE METHYL CELLULOSE

Low-substituted methyl cellulose (D.S. 0.1 to 0.9) is soluble in 2 to 10% aqueous NaOH. Such ethers are prepared by the treatment of alkali cellulose with methyl sulfate[123,124] or with methyl chloride.[19,121] Maasberg[121] prepared alkali cellulose containing a weight ratio of sodium hydroxide to cellulose of 0.35 to 0.60 by treating cellulose with 27.5 to 45% aqueous NaOH at 15° to 35°C. This alkali cellulose was reacted with a weight ratio of from 0.15 to 0.5 methyl chloride to cellulose for from 4 to 10 hrs. at 35° to 75°C. until the reaction pressure fell to zero. The products were washed with hot water containing sufficient acid to neutralize the residual sodium hydroxide and were dried. The products were soluble in 2 to 10% aqueous NaOH, but not in water. Such products are used as permanent sizing for cloth or may be formed into sheeting similar to cellophane.

[171] A. E. Broderick (to Carbide and Carbon Chemicals Corp.), U. S. Patent 2,329,741 (Sept. 21, 1943); *Chem. Abstracts*, **38**, 1112 (1944).

(j) CHEMICALLY MODIFIED METHYL CELLULOSES

Methyl cellulose is chemically modified to raise its gelation temperature, to improve its salt compatibility, to broaden its solubility, and to provide thermoplasticity.

Hydroxyethyl methyl cellulose was prepared in Germany by the successive reaction of alkali cellulose with ethylene oxide and with methyl chloride.[172,173] This product was used as a starch substitute in adhesives.

The preparation of carboxymethyl methyl cellulose, with a carboxymethoxyl D.S. of 0.2 to 0.3 and a methoxyl D.S. of 0.7 to 2.1 was described by Swinehart, Savage, and Kuhlman.[174,175] This ether approached the properties of carboxymethyl cellulose at a pH above 6 and of methyl cellulose at a pH of 2 to 4. The sodium salt was soluble in water at room temperature and remained in solution when heated to over 90°C. The salt compatibility was increased so that a technical product containing by-product salt had excellent solubility. The acid form gelled from solution at 55°C.; thus, the product could be washed with water in the acid form and then converted to the sodium form.

A hydroxypropyl methyl cellulose,[176] with 0.05 to 0.2 hydroxypropoxyl M.S. and 1.4 to 2.1 methoxyl D.S., that had a gel point of 70°C. and corresponding improved salt compatibility, was disclosed in a patent issued to Schick.[177] That this ether is more internally plasticized than is hydroxyethyl methyl cellulose is shown by a tendency toward organosolubility and thermoplasticity rather than toward increased water solubility.

6. Carboxymethyl Cellulose

Commercially, the term carboxymethyl cellulose is applied to a water-soluble cellulose ether which is actually the sodium salt of carboxymethyl cellulose. It is also frequently called cellulose gum, CMC, or sodium cellu-

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[172] D. Traill and S. Brown, *FIAT, Final Report No. 486* (Jan. 10, 1946); through Library, U. S. Department of Agriculture, Washington, D. C.

[173] M. Hagedorn and E. Rossback (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,877,856 (Sept. 20, 1932); *Chem. Abstracts*, **27**, 413 (1933).

[174] R. W. Swinehart, A. B. Savage, and W. D. Kuhlman (to The Dow Chemical Co.), U. S. Patent 2,476,331 (July 19, 1949); *Chem. Abstracts*, **43**, 9445 (1949).

[175] R. W. Swinehart (to The Dow Chemical Co.), U. S. Patent 2,510,153 (June 6, 1950); *Chem. Abstracts*, **44**, 8631 (1950).

[176] H. Dreyfus, Brit. Patent 277,721 (Sept. 30, 1927); *Chem. Zentr.*, **1928**, *I*, 445; Brit. Patent 327,157 (Mar. 28, 1930); *Chem. Abstracts*, **24**, 5157 (1930).

[177] J. L. Schick (to The Dow Chemical Co.), U. S. Patent 2,538,051 (June 16, 1951); *Chem. Abstracts*, **45**, 4489 (1951).

lose glycolate. The uses of sodium carboxymethyl cellulose stem from its properties as a protective colloid,[178] thickening agent, and film-former.

The free acid form, that is, carboxymethyl cellulose, on the other hand, has found limited application because it is, in general, not water-soluble.

Sodium carboxymethyl cellulose thickens water solutions without precipitation over a pH range of 4 to 12 and does not gel from water solutions upon heating. It is not precipitated from solution by dilute solutions of salts of alkali or alkaline earth metals; it is precipitated from solution by strong acids, by salts of amphoteric multivalent metals, and by salts of heavy metals. The protective colloid properties of sodium carboxymethyl cellulose aid in the building or promoting of detergents and in textile sizing. The physiological inertness of sodium carboxymethyl cellulose permits its use in food products.[179]

Sodium carboxymethyl cellulose is made only in relatively low ranges of substitution. At D.S. 0.7 to 1.2, it is water-soluble, yields clear solutions when purified, and is precipitated from solutions only by acidification with strong acids to pH 1 to 3. Sodium carboxymethyl cellulose of D.S. 0.3 to 0.6 is water-soluble, but is commonly sold in a technical, unpurified form; it is precipitated from solution by weak acids at pH 3. At D.S. 0.1 to 0.2 it is soluble in 3 to 10% aqueous NaOH, depending upon the extent of chilling of the solution, and in 5 to 8% NH_4OH.[180]

(a) RAW MATERIALS

The quality of the raw materials used in carboxymethylation varies with the process used, with the degree of purification of the product, and with the intended end use. The cellulose may be finely milled wood pulp,[181] purified wood pulp, or purified cotton linters.[182] The sodium hydroxide is of the same quality that is used in other cellulose etherifications. The sodium chloroacetate or chloroacetic acid used should be free of di- and trichlorinated compounds.

(b) CARBOXYMETHYLATION

Carboxymethylation differs from other cellulose etherifications in that alkali cellulose need not be prepared separately, although normally it is.

[178] C. B. Hollabaugh, L. H. Burt, and A. P. Walsh, *Ind. Eng. Chem.*, **37**, 943 (1945).

[179] H. A. Shelanski and A. M. Clark, *Food Research*, **13**, No. 1, 29 (1948).

[180] *Du Pont Sodium CMC*, E. I. du Pont de Nemours & Co., Wilmington, Del., 1947.

[181] W. F. Waldeck (to Wyandotte Chemicals Corp.), U. S. Patent 2,510,355 (June 6, 1950); *Chem. Abstracts*, **44**, 7538 (1950). R. N. Hader, W. F. Waldeck, and F. W. Smith, *Ind. Eng. Chem.*, **44**, 2803 (1952).

[182] E. D. Klug and J. Tinsley (to Hercules Powder Co.), U. S. Patent 2,517,577 (Aug. 8, 1950); *Chem. Abstracts*, **44**, 10318 (1950).

The processes used differ widely; they are based upon the experience of the manufacturers in the preparation of other materials.

The carboxymethylation reaction is:

$$R_{cell}(OH)_3 + ClCH_2COONa + NaOH \longrightarrow R_{cell}(OH)_2OCH_2COONa + NaCl + H_2O \quad (12)$$

By-product sodium glycolate formation occurs according to:

$$ClCH_2COONa + NaOH \longrightarrow HOCH_2COONa + NaCl \quad (13)$$

Technical sodium carboxymethyl cellulose contains the sodium chloride–glycolate mixture; this is removed from the purified product. It is not practical to reconvert glycolic acid to chloroacetic acid.

The traditional manufacture of sodium carboxymethyl cellulose[11,12,172] is carried out in a Werner-Pfleiderer type of mixer with toothed sigma-shaped blades and a cooling jacket. The cellulose may be steeped in sodium hydroxide (see Section F of this Chapter IX), pressed, and shredded, or the alkali cellulose may be prepared entirely in the shredder. Schmitz[183] prepared alkali cellulose in a slurry and continously removed the alkali cellulose from the slurry with the aid of press and drainage rolls. The sodium chloroacetate or chloroacetic acid may be shredded into the cellulose before the sodium hydroxide is added.

Slurry carboxymethylation in the presence of *tert*-butyl alcohol or isopropanol was disclosed by Klug and Tinsley,[182] who obtained D.S. 0.88 and a very low fiber content in the presence of these alcohols. Low substitution was obtained in the presence of methanol (D.S. 0.16) or ethanol (D.S. 0.35).

An unusual continuous carboxymethylation was disclosed by Waldeck.[181] Finely milled wood cellulose (40 to 300 mesh) was tumbled in a rotary drum and sprayed with 49% chloroacetic acid (1.27 weight ratio of acid to pulp). After thorough tumbling, sodium carbonate (0.34 sodium carbonate: pulp) was added to neutralize the chloroacetic acid. After thorough mixing, 50% NaOH solution (0.72 solution: pulp) was slowly sprayed in and the mixture was again thoroughly tumbled. When it had been dried, the technical product, D.S. 0.72, contained 1% insoluble material. The efficiency was 67%.

The principle of the alkali cellulose process of Collings and coworkers was applied to carboxymethylation by Collings, Freeman, and Anthonisen.[184] Purified cotton linters sheet was passed continuously through 75%

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[183] R. Schmitz (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,392,269 (Jan. 1, 1946); *Chem. Abstracts*, **40**, 2984 (1946).

[184] W. R. Collings, R. D. Freeman, and R. P. Anthonisen (to The Dow Chemical Co.), U. S. Patent 2,278,612 (Apr. 7, 1942); *Chem. Abstracts*, **36**, 5013 (1942).

chloroacetic acid solution (5 seconds contact time) to obtain a pickup of 0.71 weight ratio of acid:cellulose and through 41% aqueous NaOH (15 seconds contact time) to obtain a pickup of 0.98 weight ratio of sodium hydroxide:cellulose, and was shredded. A product of D.S. 0.5 to 0.6 resulted. Swinehart and Allen[185] used an additional sodium hydroxide treatment to obtain a fiber-free product of D.S. 0.6 to 1.1. Maxwell[186] prepared alkali-soluble ethers by passing the sheet continuously first through sodium hydroxide solution, and then through the etherifying agent, after which the excess was pressed out. Rogers, Mueller, and Hembree[187] prepared sodium carboxymethyl cellulose by a different continuous sheet process.

TABLE 35

Efficiency of Carboxymethylation (McLaughlin and Herbst[32])
(Mole ratio: sodium hydroxide to cellulose, 1.28:1; sodium chloroacetate to cellulose, 1.02:1)

Mole ratio, water:cellulose	Shredding time, hr.	Reaction temperature, °C.	Reaction efficiency, %	D.S.	Water solubility
0.40	1	10	25	0.31	Particles
0.40	3	10	64	0.80	Particles
0.40	6	10	67	0.84	Particles
0.75	6	25	66	0.83	Particles
1.30	6	25	69	0.86	Clear
1.50	6	25	64	0.80	Clear
3.00	6	25	31	0.39	Fibers

In most of the batch processes it is customary to transfer the reaction mass to bins, wagons, or tumbling drums for the extended reaction period after mixing is complete in order to free the expensive mixing equipment for another batch. The reaction is carried out at 0° to 70°C. The reaction may be followed by titration of the salt formed and of the sodium hydroxide present.

Efficiency of carboxymethylation was studied by McLaughlin and Herbst.[32] They found that efficiency was improved by lower reaction temperatures, by decreasing excess sodium hydroxide, and by increasing the shredding time at low water contents. The optimum water to cellulose mole ratio was 1.3 to 1. Their data are shown in Table 35.

[185] R. W. Swinehart and S. R. Allen (to The Dow Chemical Co.), U. S. Patent 2,524,024 (June 26, 1950); *Chem. Abstracts,* **45,** 1344 (1951).

[186] R. W. Maxwell (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,101,263 (Dec. 7, 1937); *Chem. Abstracts,* **32,** 1094 (1938).

[187] L. N. Rogers, W. A. Mueller, and E. E. Hembree (to Buckeye Cotton Oil Co.), U. S. Patent 2,553,725 (May 22, 1951); *Chem. Abstracts,* **45,** 8247 (1951).

(c) AFTERTREATMENT

The aftertreatment of the carboxymethylation reaction mass varies with the process. If a technical unpurified product is desired, the wet reaction mass may be neutralized with sodium bicarbonate, shredded, and sold wet,[172,180,188,189] or the technical product may be dried and sold.[180,181] The technical products are of D.S. 0.3 to 0.7 and of low intrinsic viscosity. Typical compositions of the technical products are shown in Table 36.[190,191]

TABLE 36

Composition of Typical Technical Sodium Carboxymethyl Celluloses, D.S. 0.7 (The Wyandotte Chemicals Corp.[190] and Hercules Powder Company[191])

Ingredient	Composition, weight ratio to sodium carboxymethyl cellulose	
	A[190]	B[191]
Sodium carboxymethyl cellulose	1.0	1.0
Water	0.08	0.05
Sodium chloride	0.26	0.04
Sodium carbonate	0.03	—
Sodium carboxymethyl cellulose (low D.P.) plus sodium glycolate	0.15	0.02

(d) PURIFICATION

Products of D.S. 0.5 to 1.2 may be fiber free and can be purified to yield clear solutions. Purification methods involve either the use of alcohol–water mixtures to extract the salt and the sodium glycolate without solution of the sodium carboxymethyl cellulose, or conversion to the insoluble acid form or to an insoluble salt.

Collings, Freeman, and Anthonisen[184] neutralized the reaction mass, D.S. 0.6, with hydrochloric acid, dissolved the acid form, precipitated it with alcohol, and washed it with aqueous alcohol. Klug and Tinsley[182] washed the product of their alcohol slurry process, D.S. 0.88, with 70% aqueous methanol. Swinehart and Allen[185] and Houghton[192] used similar methods.

[188] *Wyandotte Carbose*, Wyandotte Chemicals Corp., Wyandotte, Mich., 1952.

[189] *Hercules CMC Cellulose Gum*, Hercules Powder Co., Wilmington, Del., 1949 and 1951.

[190] Wyandotte Chemicals Corp., Wyandotte, Mich., unpublished data.

[191] Hercules Powder Co., Wilmington, Del.

[192] A. A. Houghton (to Imperial Chemical Industries, Ltd.), U. S. Patent 2,513,725 (July 4, 1950); *Chem. Abstracts*, **44**, 8656 (1950).

Freeman and Anthonisen[193] and Houghton[194] converted sodium carboxymethyl cellulose to the acid form by treatment with strong acid below pH 1.

A unique method of reducing the amount of acid required to convert to the acid form was disclosed by Lamborn.[195] Crude product containing 20% sodium carboxymethyl cellulose (D.S. 0.7), 33% salt, and 47% water was neutralized to pH 6.5 with sodium bisulfate in a Werner-Pfleiderer mixer. The crude neutral dough was extruded through orifices in a press to form strands of diameter 0.038 in. The strands were dried to below 5% moisture in warm air, and were immersed for 2 hrs. or more in a bath kept at pH 1 with hydrochloric acid. The strands were then washed with water until free of contaminating salts, dried, and granulated.

Freeman and Roberts[196] recovered carboxymethyl cellulose as its alkali-soluble aluminum salt.

(e) CARBOXYMETHYL CELLULOSE BASE FLAKE

Sodium carboxymethyl cellulose is a light cream to white powder. It browns upon heating at 180° to 225°C. and chars upon heating to 210° to 250°C. It is soluble in cold and in warm water. It is highly moisture-absorbent and may gain its own weight of water at high humidity.[197] Bulk densities range from 0.4 to 0.8 g./ml.

(f) CARBOXYMETHYL CELLULOSE SOLUTIONS

Sodium carboxymethyl cellulose dissolves in efficiently agitated water, and in aqueous ethanol or aqueous acetone containing over 60% water. Solution clarity is improved by passing the solutions through a colloid mill or a homogenizer.

Solutions of sodium carboxymethyl cellulose are thixotropic, and their viscosities depend upon the rate of shear and other variables, so the viscosity is usually measured under specified conditions with a rotational viscometer such as the Brookfield. Figure 68 shows the relation of solution viscosity to concentration for sodium carboxymethyl cellulose.

Intrinsic viscosity values can be obtained for solutions of sodium carboxymethyl cellulose in 5% NaOH solution, in which case Martin's constant varies from 0.14 to 0.16. For example, low-, medium-, and high-

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[193] R. D. Freeman and R. P. Anthonisen (to The Dow Chemical Co.), U. S. Patent 2,351,258 (June 13, 1944); *Chem. Abstracts*, **38**, 5405 (1944).

[194] A. A. Houghton and K. J. C. Luckhurst (to Imperial Chemical Industries, Ltd.), U. S. Patent 2,357,469 (Sept. 5, 1944); *Chem. Abstracts*, **39**, 416 (1945).

[195] B. T. Lamborn (to Hercules Powder Co.), U. S. Patent 2,513,807 (July 4, 1950); *Chem. Abstracts*, **44**, 8656 (1950).

[196] R. D. Freeman and M. J. Roberts (to The Dow Chemical Co.), U. S. Patents 2,331,858 and 2,331,859 (Oct. 12, 1943); *Chem. Abstracts*, **38**, 1641 (1944).

[197] C. J. Brown and A. A. Houghton, *J. Soc. Chem. Ind. (London)*, **60**, 254T (1941).

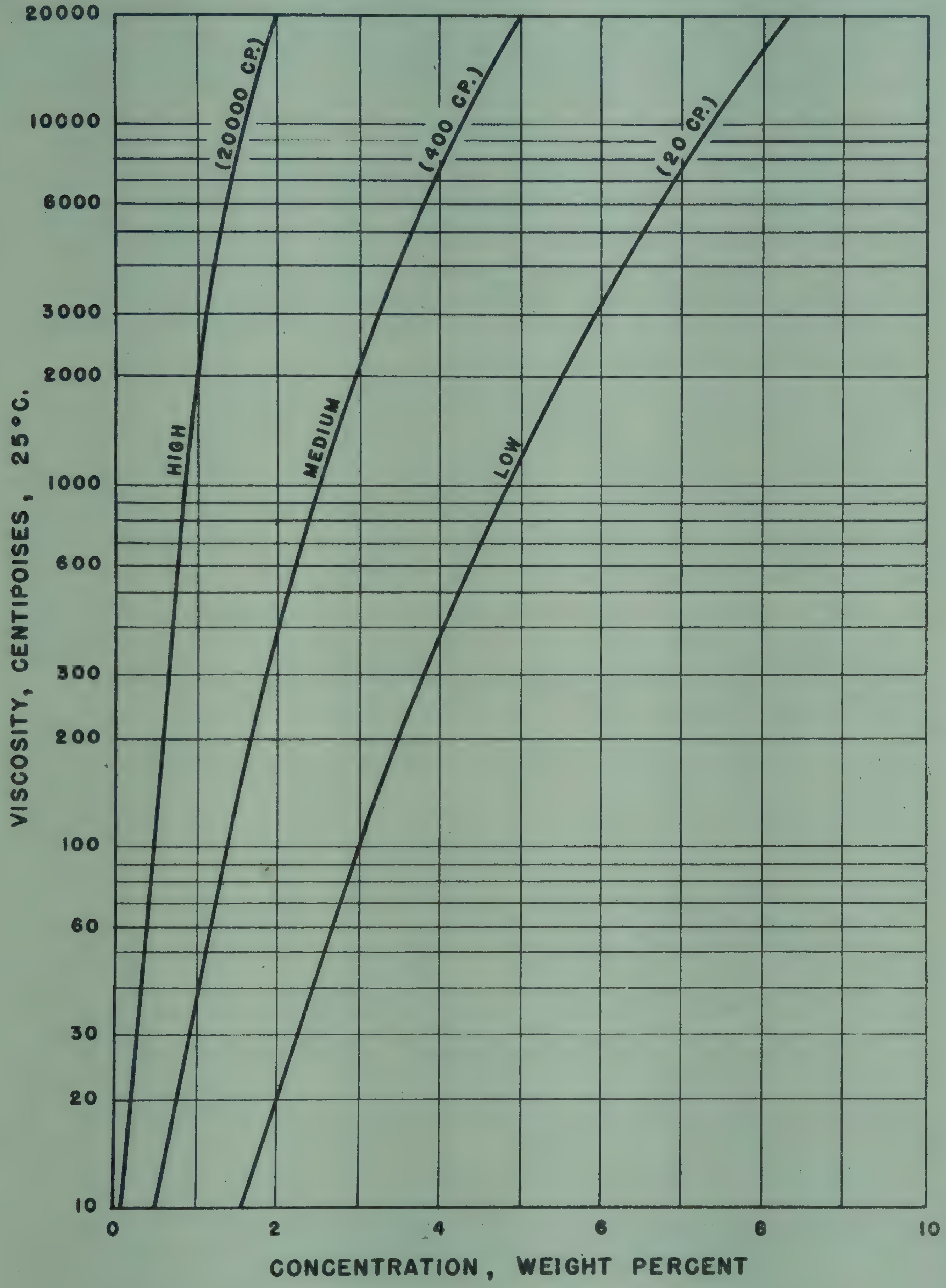

Fig. 68. Sodium carboxymethyl cellulose: viscosity–concentration chart (Hercules Powder Co.[189]). Viscosities in 2% solution in water at 25°C. are shown in parentheses on the curves.

viscosity types of sodium carboxymethyl cellulose of D.S. 0.8 give intrinsic viscosities of the order of 1.5 to 2.0, 2.0 to 2.5, and 5 to 9, respectively.[191]

When sodium carboxymethyl cellulose solutions are heated, the viscosity decrease with increasing temperature is reversible if the maximum temperature is not over 50°C.; above this temperature a permanent viscosity loss may occur.[189,197,198] Such viscosity loss is more pronounced in the presence of alkali, for solutions of alkali-soluble material lose viscosity at room temperature. The relation of solution viscosity to pH is shown in Figure 69.

Carboxymethyl cellulose is a weak acid ($K_{\text{ionization}} = 3 \times 10^{-5}$). The pH of precipitation of the acid form varies with D.S.; thus D.S. 0.1 to 0.2 precipitates below pH 6; D.S. 0.3 to 0.5 below pH 3; and D.S. 0.7 to 0.9 below pH 1. The pH of precipitation also varies to some extent with the acid used. The acid form of carboxymethyl cellulose becomes insoluble if overdried, and redissolves only in dilute alkalies.[12,199] Chowdhury[12] attributed this behavior to inner lactone formation. A water dispersion of the free acid can be made by treatment with ion-exchange resins.[189]

The salt compatibility of sodium carboxymethyl cellulose solutions varies with the metallic ion present.[189] When solutions containing 1% sodium carboxymethyl cellulose and 5% of various salts were prepared, the results observed were:

	Precipitate	
No precipitate	Soluble in NaOH	Insoluble in NaOH
$Ba(NO_3)_2$(thixotropic)	$Al_2(SO_4)_3$	$Cr(NO_3)_3$
$CaCl_2$	$BaCl_2$	$AgNO_3$
$MgCl_2$	$SnCl_2$	$FeCl_3$
$MnSO_4$		$FeSO_4$
		$Pb(CH_3CO_2)_2$

(g) CARBOXYMETHYL CELLULOSE SHEETING

Sodium carboxymethyl cellulose sheeting can be cast from water solutions and is unaffected by most solvents and oils. The physical properties of such sheeting are markedly dependent on the relative humidity. At 50% relative humidity, the unplasticized film has a tensile strength of 10,000 to 12,000 lb./sq. in., has 3% elongation, and endures 200 M.I.T. double folds. At higher humidity, the film becomes weaker and more flexible. The addition of about 20% plasticizer (such as glycerin or ethylene glycol) will also modify the film properties. Such sheeting has a tensile strength of 7000 lb./sq. in., has 15% elongation, and endures 1000 M.I.T. double folds.

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[198] *Carboxymethocel,* The Dow Chemical Co., Midland, Mich., 1945.

[199] I. Sakurada, *Z. angew. Chem.,* **42,** 640 (1929).

(h) INCREASING WATER RESISTANCE

The water resistance of sodium carboxymethyl cellulose sheeting and coatings can be increased by setting the sheeting to relative insolubility by salt (for example, alum) treatment or acid treatment, or by cross-linking with urea–formaldehyde or melamine–formaldehyde resins.

(i) COMPATIBILITY

Sodium carboxymethyl cellulose is compatible in solution with many compounds, but shows limited compatibility in sheeting. It is compatible with formamide, hydroxyethyl cellulose, natural gums, pectin, polyvinyl alcohol, sodium alginate, starch, and urea–formaldehyde resins.

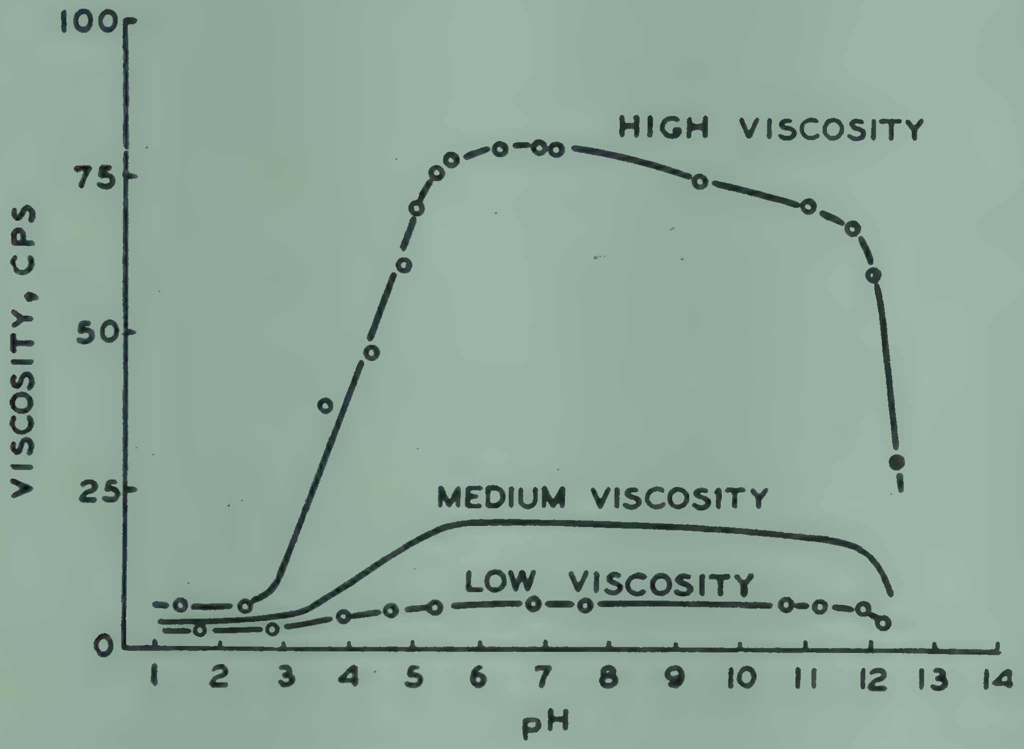

Fig. 69. Carboxymethyl cellulose: variation of solution viscosity with pH (Brown and Houghton[197]). Viscosities in 1% solution in water at 25°C.

7. Hydroxyethyl Cellulose

Although no sodium hydroxide is consumed directly during the preparation of hydroxyethyl cellulose from ethylene oxide, sodium hydroxide is necessary in order to swell the cellulose and to catalyze the reaction. Ethylene chlorohydrin is also a suitable reagent for hydroxyethylation.

The uses of hydroxyethyl cellulose result from its solubility in cold and hot water, its salt and solvent compatibility, and its effectiveness as a protective colloid. Hydroxyethyl cellulose thickens solutions over a wide range of pH without precipitation.

In hydroxyethyl cellulose preparation, substitution takes place both on the cellulose hydroxyls (the conventional D.S.) and by chain polymerization on the hydroxyls of previously substituted groups. The average number of moles of alkene oxide consumed that become attached to a glucopyranose residue in these two ways is termed M.S.[107]

Hydroxyethyl cellulose is made only in relatively low ranges of substitution. Hydroxyethyl cellulose of M.S. 0.50 or higher is water-soluble; hydroxyethyl cellulose of M.S. 0.05 to 0.4 is soluble in aqueous alkali solutions. The lower substituted ethers are soluble only upon freezing.

(a) HYDROXYETHYLATION

Much of the previous discussion of carboxymethyl cellulose applies also to hydroxyethyl cellulose. The quality of the materials used varies with the degree of purification of the product and with the intended end use. Hydroxyethyl cellulose may be prepared by the reaction of alkali cellulose with ethylene oxide or with ethylene chlorohydrin (2-chloroethanol); the chlorohydrin probably is converted to the oxide, and the oxide then reacts with the alkali cellulose.

Hydroxyethylation was studied by Morgan[33] (see Table 18), who showed the relation of ethylene oxide consumption to reaction efficiency, solubility, and M.S., by Tasker and Purves,[106] and by Cohen and Haas,[107] who presented partial analyses of hydroxyethyl celluloses (see Tables 19 and 20). The probable structure of hydroxyethyl cellulose is indicated in Figure 59. The formation of hydroxyethyl cellulose is shown in equations 2, 3, and 4. These reactions take place in the presence of sodium hydroxide and water.

Davis[200] hydroxyethylated cotton linters in the presence of benzene or ethyl ether as a carrier. He found that for alkali-soluble products the optimum range of the ratio of sodium hydroxide to cellulose was 0.5:1 to 1.0:1, and the optimum range of the ratio of water to cellulose was 1.0:1 to 2.0:1. He found also that for the production of uniformly substituted ethers it was best to limit the ratio of ethylene oxide to cellulose to approximately 0.25:1. Uniform additional substitution was then obtained by further treatments with ethylene oxide.[200,201]

Schorger[131,132] and Shoemaker[132] prepared low-substituted alkali-soluble hydroxyethyl cellulose and studied the effect of sodium hydroxide concentration and of freezing upon the solubility of the products. They steeped cellulose in 30% NaOH and pressed it to a sodium hydroxide:cellulose ratio of 0.9:1 and a water:cellulose ratio of 1.5:1. They found that the solubility of such alkali-soluble ethers is greater in 8% NaOH than in higher or lower concentrations. They obtained optimum filterability when they froze solutions containing 5 to 6% NaOH.

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[200] W. E. Davis, Dissertation, New York State College of Forestry, Syracuse, N. Y., 1941.

[201] F. H. Reichel and R. T. K. Cornwell (to Sylvania Industrial Corp.), U. S. Patent 2,388,764 (Nov. 31, 1945); *Chem. Abstracts*, **40**, 1656 (1946).

Reichel and Hindry[202] prepared alkali cellulose by the viscose method (see Section F of this Chapter IX) by treating cellulose with 18% NaOH, pressing, and shredding. The crumbs were then etherified to M.S. 0.3, and the excess etherifying agent was used up by the addition of regenerated cellulose. The product was soluble in 10% NaOH at 0°C.

Hydroxyethyl cellulose may also be made by a slurry method[203] and by a vacuum process.[204]

(b) AFTERTREATMENT

The aftertreatment of the reaction mass varies with the process and with the end use. The residual sodium hydroxide must be neutralized in order to prevent viscosity degradation. Alkali-soluble ethers may be washed with acid and then with water after neutralization is complete, and dried.

Water-soluble ethers are difficult to purify. Both the alkali-soluble and the water-soluble ethers may be dried after neutralization and sold as technical products, or they may be dissolved and sold in solution form. Solutions may be purified by dialysis.

Kunz[205] proposed the addition of material that would form a solid hydrate in order to take up water and neutralize simultaneously. Crude reaction mass (sodium hydroxide:cellulose 0.33:1, water:cellulose 1.47:1) was mixed with phosphoric acid (phosphoric acid:cellulose 0.66:1; water:cellulose 0.12:1). The temperature rose to 50°C. during mixing. The product was dried below 35°C., then raised to 100°C. The product was a mixture of hydroxyethyl cellulose and hydrated sodium phosphate of pH 8.4.

Aluminum sulfate, esters, alcohols, or ketones may be used to reduce solubility during the washing of hydroxyethyl cellulose.

(c) HYDROXYETHYL CELLULOSE BASE FLAKE

Water-soluble hydroxyethyl cellulose, M.S. over 0.5, is a white to light tan powder, soluble in water over a wide temperature range. It slowly decomposes at temperatures over 100°C., especially in the presence of acids, alkalies, or salts. It browns at about 180°C. and chars upon continued heating at over 200°C. Alkali-soluble hydroxyethyl cellulose, like other alkali-soluble ethers, is a white fibrous material similar to the original cellulose.

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[202] F. H. Reichel and W. F. Hindry (to Sylvania Industrial Corp.), U. S. Patent 2,172,-109 (Sept. 5, 1939); *Chem. Abstracts*, **34**, 262 (1940).

[203] E. D. Klug and H. G. Tennent (to Hercules Powder Co.), U. S. Patent 2,572,039 (Oct. 23, 1951); *Chem. Abstracts*, **46**, 1256 (1952).

[204] D. R. Erickson, U. S. Patent 2,469,764 (May 10, 1949); *Chem. Abstracts*, **43**, 5592 (1949).

[205] W. B. Kunz (to American Viscose Corp.), U. S. Patent 2,488,631 (Nov. 22, 1949); *Chem. Abstracts*, **44**, 1702 (1950).

(d) HYDROXYETHYL CELLULOSE SOLUTIONS

Water-soluble hydroxyethyl cellulose is soluble in efficiently agitated water. It is slightly soluble upon heating (up to 1%) in ethylene glycol, propylene glycol, and glycerol, and (5%) in N-acetylethanolamine.[206] Solutions are opalescent in appearance.

Water-soluble hydroxyethyl cellulose is compatible in solution with starch and starch derivatives, gelatin, natural gums, and sodium carboxymethyl cellulose, but is only partly compatible with methyl cellulose and polyvinyl alcohol. Aqueous solutions tolerate up to equal parts by weight of the water-soluble alcohols and much larger quantities of polyhydroxy compounds, carboxylic acids, aldehydes, and amines without gelation. Low concentrations of water-soluble esters and ketones have a precipitating effect. Of the common salts, only the sulfates affect solution stability and only aluminum sulfate has a precipitating effect.

The viscosity of solutions of water-soluble hydroxyethyl cellulose is lowered by dilute strong acids and by concentrated formic acid. Alkali causes a slower viscosity decrease.

Alkali-soluble hydroxyethyl cellulose is soluble, depending upon its degree of substitution, in 2 to 10% NaOH, in 10% KOH, and in alkaline 40% urea.[207]

(e) HYDROXYETHYL CELLULOSE SHEETING

Water-soluble hydroxyethyl cellulose solutions yield clear sheeting that is heat stable below 100°C. and is soluble in water, but insoluble in most organic solvents. The flexibility of sheeting is increased by plasticization with 10 to 50% (based upon the ether) of sorbitol, glycols, liquid polyglycols, higher diols, N-acetylethanolamine, or sulfonated castor oil.

Alkali-soluble hydroxyethyl cellulose, like other alkali-soluble ethers, yields sheeting from aqueous NaOH solutions that can be set by flooding with water or by neutralization with acid or with salt solutions. Such sheeting is reported[207] to have a tensile strength of 13,000 lb./sq. in., and an elongation of 6%, and to withstand 1300 M.I.T. double folds.

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[206] *"Cellosize" Hydroxyethylcellulose*, Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corp., New York, F5339-D.

[207] W. E. Gloor, B. H. Mahlman, and R. D. Ullrich, *Ind. Eng. Chem.*, **42**, 2150 (1950).

Alkali-soluble hydroxyethyl cellulose is compatible with gelatin, carboxymethyl cellulose, methyl cellulose, and casein.

(f) IMPROVING WATER RESISTANCE

Water resistance (partial in the case of treated, water-soluble hydroxyethyl cellulose) is improved by treatment before drying with glyoxal,[171] urea–formaldehyde, or melamine–formaldehyde. Both types are rendered photosensitive by chromates and by azo dyes and may then be rendered temporarily insoluble by exposure to ultraviolet light.[206,207] The acetal of glyoxal and hydroxyethyl cellulose hydrolyzes upon standing in water.[206]

(g) MIXED HYDROXYETHYL ETHERS

The addition of a small amount of hydroxyethyl substitution (0.3 to 0.4 M.S.) to conventional derivatives confers certain unusual properties; thus the salt precipitation of methyl cellulose and carboxymethyl cellulose is reduced, the aliphatic-solvent tolerance of high-substituted ethyl cellulose is increased, and the acetone solubility of high-substituted cellulose acetate is increased.[207a,208]

8. Benzyl Cellulose

Benzyl cellulose, which results from the reaction of alkali cellulose with benzyl chloride, has reached commercial production in Europe, but has not passed beyond the pilot plant stage in the United States.

Benzyl cellulose is internally plasticized to an extent that it may be used for coatings, plastics, and lacquers without the addition of plasticizer. It is soft, but water resistant.

(a) BENZYLATION

Lorand and Georgi[26,209] prepared benzyl cellulose with minimum agitation and carried out continuous water removal in order to improve efficiency. They followed the course of the benzylation with successive photographs (Fig. 70). Benzylation began at active spots upon the fiber surface (Fig. 70A) and moved inward from one growth layer to the next. Figure 70B shows drops of weak salt–sodium hydroxide solution leaving the water-

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[207a] Klug, E. D. (to Hercules Powder Co.), Brit. Patent 670,672 (April 23, 1952); *Chem. Abstracts*, **46**, 8372 (1952); U. S. Patent 2,618,632 (Nov. 18, 1952).

[208] M. Hagedorn and P. Möller (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,994,038 (May 12, 1935); *Chem. Abstracts*, **29**, 3156 (1935); A. E. Broderick (to Carbide and Carbon Chemicals Corp.), U. S. Patent 2,330,263 (Sept. 28, 1943); *Chem. Abstracts*, **38**, 1365 (1944).

[209] E. J. Lorand (to Hercules Powder Co.), U. S. Patent 2,056,324 (Oct. 6, 1936); *Chem. Abstracts*, **30**, 8615 (1936).

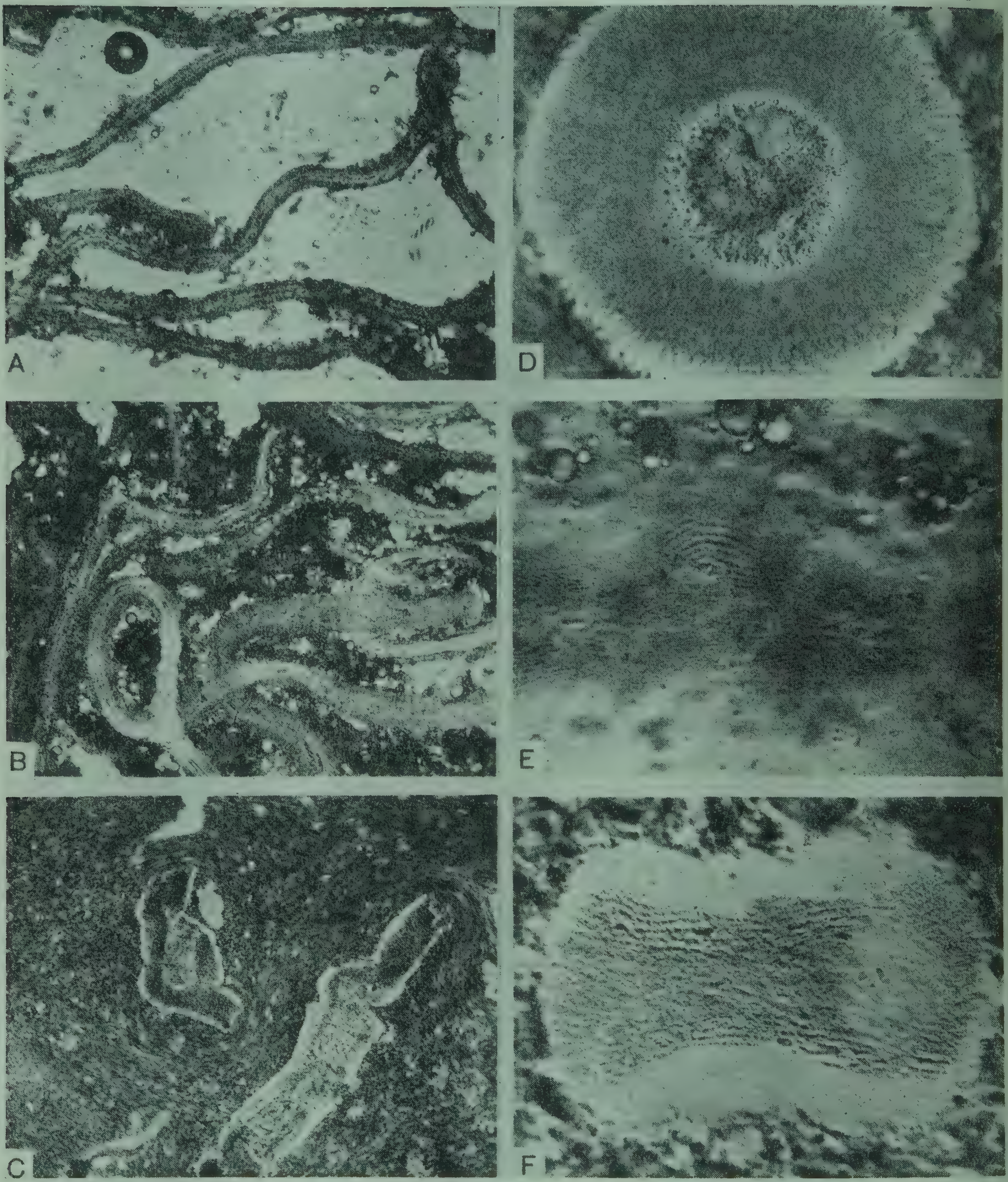

Fig. 70. Benzyl cellulose: stages in benzylation (Lorand and Georgi[26]). *A* and *B*, fibers at early stages of benzylation (magnification ×90); *C*, benzylated fibers breaking up as gel sheath dissolves (magnification ×90); *D* and *E*, sections through benzylated fiber at an advanced stage of benzylation (magnification ×350); *F*, section through benzylated fiber showing gelation of outer layers (magnification ×350).

pellent benzylated areas. Figures 70D and 70E show in section the migra- n of weak salt–sodium hydroxide solution from the benzylated outer ers to the fiber core. Figure 70F shows in section a fiber half benzylated d swollen, but not dissolved in benzyl chloride. Figure 70C shows nzylated fibers breaking up as their outer layers dissolve.

The benzylation reaction and the by-product reactions are analogous to uations 6, 7, and 8.

Gomberg and Buchler,[14] who benzylated at low temperatures in the pres- ce of low sodium hydroxide concentrations, prepared benzyl cellulose that s only partially soluble. Okada[210] prepared benzyl cellulose under reflux; obtained a soluble product from a low sodium hydroxide concentration. found that ethers prepared rapidly at high temperature had better echanical properties than did products of a slow, low-temperature reac- n.

Brandt[211] mercerized cellulose in 16 to 18% aqueous sodium hydroxide d removed the excess sodium hydroxide by strong pressing. His benzyl- ed products were not completely soluble and his reaction rates decreased pidly. He found it necessary to resort to sodium hydroxide stronger than % or to continuous water removal, to obtain D.S. 2.0 or higher. His scosities were low.

Mienes[212] found that the solubility of benzyl cellulose increased in pro- rtion to the squeezing pressure at a given sodium hydroxide to cellulose tio. At substitution below D.S. 2.0, the D.S. was said to be a function the sodium hydroxide:cellulose ratio; at high substitutions this ratio s said to be of decreasing influence. He recommended sodium hydroxide dition[213,214] to keep the sodium hydroxide concentration constant. D.S.) resulted from alkali cellulose prepared from 22% NaOH.

In German benzyl cellulose manufacture,[172,215] alkali cellulose (weight tio of sodium hydroxide:cellulose, 2.65:1; of water:cellulose, 4.20:1), epared in a Werner-Pfleiderer mixer, was reacted with benzyl chloride

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[210] H. Okada, *Cellulosechemie*, **12**, 11 (1931).

[211] K. Brandt, Dissertation, Berlin, 1932; through K. Mienes, *Celluloseester und Cellu- eäther*, Chemisch-technischer Verlag Dr. Bodenbender, Berlin-Steglitz, 1934.

[212] K. Mienes, *Celluloseester und Celluloseäther*, Chemisch-technischer Verlag Dr. denbender, Berlin-Steglitz, 1934.

[213] G. von Frank and K. Mienes, German Patent 555,930 (Aug. 1, 1932); *Chem. Ab- acts*, **26**, 6134 (1932).

[214] G. von Frank and K. Mienes, German Patent 575,349 (Apr. 27, 1933); *Chem. Ab- acts*, **27**, 5974 (1933).

[215] I.G. Farbenindustrie Akt.-Ges., German Patent 492,062 (Feb. 15, 1930); *Chem. stracts*, **24**, 2599 (1930).

(ratio to cellulose 4.85:1) in an autoclave at 70° to 110°C. for 8 hrs. with stirring. The excess sodium hydroxide solution was then drained off for re-use, and the product was washed with water to remove salt and with methanol to remove organic by-products, washed again with water, and dried. Benzyl cellulose, D.S. 2.0 (benzyl cellulose:cellulose 1.9:1) and by-products (benzyl alcohol plus benzyl ether:cellulose 2:1) resulted.

Lorand[216] decreased by-product formation by the addition of benzyl ether to the charge. Mienes[212] proposed the use of chlorobenzene as a solvent for low-substituted benzyl cellulose in the early stages of the reaction; Savage[19] used benzene as a diluent; Huber[217] used tertiary amines as dispersants. The patent literature was reviewed by Worden[7] and by Mienes.[212]

(b) PURIFICATION

Purification by extraction with water and with alcohols has already been described.[172,215] Dörr[218] disclosed the addition of such soaps as sodium oleate to the crude product and precipitation of the mixture as a flocculent, easily washable powder. Lorand[219] dispersed the crude product in such solvents as ethers, high water-soluble alcohols, and hydrocarbon–alcohol mixtures that had a high separation ratio and a low breakup ratio upon precipitation. Savage[19] washed the crude reaction solution by countercurrent liquid–liquid extraction with an aqueous alcohol.

(c) BENZYL CELLULOSE BASE FLAKE[220]

Benzyl cellulose is a white, granular material of specific gravity 1.2. The melting point of benzyl cellulose varies from 90° to 155°C. depending upon degree of substitution and viscosity (see Fig. 60). Benzyl cellulose is soluble in higher aliphatic and cyclic ketones, esters, lower aromatic hydrocarbons, chlorinated hydrocarbons, and aromatic hydrocarbon–alcohol mixtures.

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[216] E. J. Lorand (to Hercules Powder Co.), U. S. Patent 2,001,102 (May 14, 1935); *Chem. Abstracts*, **29**, 4580 (1935).

[217] Eugen Huber (to I. G. Farbenindustrie Akt.-Ges.), U. S. Patent 1,805,365 (May 12, 1931); *Chem. Abstracts*, **25**, 3832 (1931).

[218] E. Dörr (to Hercules Powder Co.), U. S. Patent 2,020,934 (Nov. 12, 1935); *Chem. Abstracts*, **30**, 613 (1936).

[219] E. J. Lorand (to Hercules Powder Co.), U. S. Patent 2,056,612 (Oct. 6, 1936); *Chem. Abstracts*, **30**, 8615 (1936).

[220] *Benzyl Cellulose*, Hercules Powder Co., Wilmington, Del., 1944.

(d) BENZYL CELLULOSE SHEETING[220]

The properties of benzyl cellulose sheeting are shown in Table 37. The electrical properties of benzyl cellulose are similar to those of ethyl cellulose. The tensile strength of benzyl cellulose is lower than that of other cellulose derivatives. The light and heat stability are low. The low-temperature flexibility of benzyl cellulose is comparable to that of ethyl cellulose.

TABLE 37

Properties of Benzyl Cellulose Sheeting
(Hercules Powder Company[220])

Property	Value, unplasticized benzyl cellulose, 0.003-in. film
Tensile strength, lb./sq. in.	6700
Flexibility, 25°C., M.I.T. double folds	350
Elongation, %	19
Moisture permeability, g./sq. m./24 hrs. at 35°C.	82
Fade-Ometer	
hours to embrittlement	24
hours to discolor	24

(e) BENZYL CELLULOSE PLASTICS[220]

The properties of unplasticized benzyl cellulose plastics are shown in Table 38. The softeness and low moisture absorption of benzyl cellulose are evident from the table.

TABLE 38

Properties of Benzyl Cellulose Plastics (Hercules Powder Company[220])
Benzyl cellulose, D.S. 2.3; viscosity, 70 cps.; ash, 0.11%; stabilized with 1% diphenyl amine

Test	Method	Extrusion	Injection
Flow temperature, °F.	D569-41T	—	220[a]
Rockwell M hardness	D229-39	49	46
Charpy impact, ft.-lb./inch notch	D256-41T	0.5	1.6
Water absorption, %	D570-40T	0.54	0.44
Heat distortion temperature, °C.	—	47	—
Izod impact, ft.-lb./inch notch	—	1.6	—
Cylinder temperature, °F.	—	—	385
Nozzle temperature, °F.	—	—	385
Mold temperature, °F.	—	—	100
Mold pressure, lb./sq. in. gage	—	—	9000

[a] 100 lb./sq. in.

(f) COMPATIBILITY[220]

Benzyl cellulose is compatible with many resins, with most common plasticizers, and with polystyrene.[19] It is incompatible with other cellulose esters and ethers and with other vinyl polymers.

9. Addition to Cellulose of Olefins Activated by Polar Substituent Groups

(a) THEORY

The rate of addition of a reagent to an olefinic double bond is influenced[221] by the position of the double bond with respect to the rest of the molecule, by the nature of the other groups present, and by the catalyst and the solvent that are used. Anionoid reagents do not usually react with the double bond in olefins, because the double bond cannot act as an electron acceptor; but, if an activating substituent group is conjugated with the double bond, anionoid addition may occur. Thus Michael[222] showed that α,β-unsaturated esters and ketones combined with malonic ester and the like under the influence of sodium ethoxide. Bruson and Riener[223] showed that, if alkaline catalysts are present, acrylonitrile will add to polyhydric alcohols according to the mechanism:

$$\bar{X} + \overset{\curvearrowright}{CH_2{=}}CHCN \longrightarrow XCH_2\bar{C}HCN \xrightarrow{H^+} XCH_2CH_2CN \qquad (14)$$

where $\bar{X}$ is an anionoid reagent. Hydroxyl groups attract protons, causing negative ion formation, so that alkaline catalysis is necessary.

Although the earliest literature references to the addition of activated olefins to cellulose concerned the preparation of sulfoethyl cellulose from cellulose and vinylsulfonic acid,[39] most of the literature describes the use of acrylonitrile with cellulose to obtain cyanoethyl cellulose, or its hydrolytic product, carboxyethyl cellulose.

(b) CYANOETHYLATION

Acrylonitrile cyanoethylates the hydroxyls of cellulose in the presence of alkali. If uniform products are desired, the cellulose should pass into solution early in the reaction. For this reason viscose is usually used as the starting material. The technical uses of cyanoethyl cellulose include the preparation of water-soluble yarns, twistless yarns, and the modification of "brushed rayon."[224,225]

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[221] W. J. Hickinbottom, *Reactions of Organic Compounds*, 2d ed., Longmans Green, London, 1948, p. 35.

[222] A. Michael, *J. prakt. Chem.*, **35**, 349 (1887); **37**, 496 (1889).

[223] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **64**, 2850 (1942); **65**, 18, 23 (1943); **66**, 56 (1944).

If strong alkali or long reaction times are used, the cyanoethyl cellulose will be hydrolyzed to carboxyethyl cellulose. Hydrolysis of cyanoethyl cellulose with boiling 5 to 10% aqueous NaOH gives carboxyethyl cellulose, but splitting occurs at the ether linkage and ammonia is liberated. The cellulosic hydrolysis product contains no nitrogen, but the carboxyl groups present are equivalent to only about one-fourth of the nitrogen liberated as ammonia.

The reactions include:

$$\underset{\text{Cellulose}}{R_{cell}OH} + \underset{\text{Acrylonitrile}}{CH_2{=}CHCN} \xrightarrow{NaOH} \underset{\text{Cyanoethyl cellulose}}{R_{cell}OCH_2CH_2CN} \tag{15}$$

$$R_{cell}OCH_2CH_2CN \xrightarrow{H_2O} \underset{O\text{-Carbamylethyl cellulose}}{R_{cell}OCH_2CH_2CONH_2} \tag{16}$$

$$R_{cell}OCH_2CH_2CONH_2 \xrightarrow{H_2O} \underset{\text{Carboxyethyl cellulose}}{R_{cell}OCH_2CH_2COOH} + NH_3 \tag{17}$$

$$R_{cell}OCH_2CH_2CN \longrightarrow R_{cell}OH + CH_2{=}CHCN \tag{18}$$

In practice it is found that the nitrogen content rises to a maximum and then falls. Some water-soluble derivatives[226] contained less than 10% carboxyethyl groups, whereas lower or higher substituted ethers contained none.

The cyanoethylation reaction is very sensitive to temperature changes.[224–227] Hydrolysis is appreciable at temperatures above 15°C. At a given temperature, the degree of cyanoethylation increases as the mole ratio of acrylonitrile to cellulose increases. The maximum degree of cyanoethylation is reached in about 4 hours, and it decreases thereafter.

Increasing the sodium hydroxide concentration increases the rates both of cyanoethylation and of hydrolysis, so that the net result is a lower degree of cyanoethylation. The rate of cyanoethylation can be increased by increasing the caustic ratio, if the temperature is kept down to 10°C.

The hydrolytic side reactions of acrylonitrile contribute to inefficiency.

$$CH_2{=}CHCN + H_2O \longrightarrow \underset{\text{Hydracrylonitrile}}{HOCH_2CH_2CN} \tag{19}$$

$$HOCH_2CH_2CN + CH_2{=}CHCN \longrightarrow \underset{\text{Bis}(\beta\text{-cyanoethyl) ether}}{NCCH_2CH_2OCH_2CH_2CN} \tag{20}$$

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[224] J. H. MacGregor and C. Pugh, *J. Soc. Dyers Colourists*, **67**, 66, 74 (1951).

[225] J. A. Somers, *British Rayon & Silk J.*, **26**, No. 312, 67 (1950).

[226] F. Happey and J. H. MacGregor, *Nature*, **160**, 907 (1947).

[227] J. H. MacGregor and C. Pugh, *The Reaction of Acrylonitrile with Polysaccharides*, 11th International Congress of Pure and Applied Chemistry, London, 1947, in press.

Further hydrolysis proceeds in the same manner that was given above for the cellulose ether.

$$\underset{}{CH_2{=}CHCN} + H_2O \longrightarrow \underset{\text{Acrylamide}}{CH_2{=}CHCONH_2} \qquad (21)$$

$$CH_2{=}CHCONH_2 + NaOH \longrightarrow \underset{\text{Sodium acrylate}}{CH_2{=}CHCOONa} + NH_3 \qquad (22)$$

(c) ALKALI-SOLUBLE CYANOETHYL CELLULOSE

When the mole ratio of acrylonitrile to cellulose is 0.5:1 to 1.2:1, and the sodium hydroxide concentration is below 15%, the cyanoethyl celluloses that are obtained (D.S. 0.2 to 0.3, nitrogen below 2%) are insoluble in water, but are soluble in dilute aqueous solutions of sodium hydroxide or of quaternary ammonium bases, and in 25 to 50% solutions of ammonium thiocyanate or zinc chloride. These ethers are spun into yarns, which take up 200 to 300% water, but do not dissolve in water.

(d) WATER-SOLUBLE CYANOETHYL CELLULOSE[42,228]

When the mole ratio of acrylonitrile to cellulose is from 1.5:1 to 4:1, and the sodium hydroxide concentration is below 10%, the cyanoethyl celluloses that are produced (D.S. 0.7 to 1.0, nitrogen up to 7%) are soluble in acid, neutral, or alkaline aqueous solutions. These solutions may be purified by dialysis, and the ethers may then be precipitated by acetone or by ethanol. The neutral solutions do not have a gel temperature when heated. These ethers form transparent sheeting, and are emulsifying agents and nonionic surface-active agents.

When the mole ratio of acrylonitrile to cellulose exceeds 4:1, a second series of water-insoluble, alkali-soluble products results. The products are less soluble in caustic solution as the D.S. is increased, but at D.S. 2.0 they become soluble in 50:50 acetone:water.

TABLE 39

Cyanoethyl Cellulose: Relation of Mole Ratio of Acrylonitrile to Cellulose and Degree of Substitution (Somers[225])

Mole ratio:acrylonitrile:cellulose	1.4	1.5	1.6	12.0
Degree of substitution	1.0	1.2	1.4	1.7

Table 39 shows that the substitution is increased rather little by an increase in the ratio of acrylonitrile to cellulose. Table 40 shows the increase

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[228] J. H. MacGregor and Courtaulds, Ltd., Brit. Patent 588,751 (July 2, 1947); *Chem. Abstracts*, **41**, 6718 (1947); Brit. Patent 636,020 (April 19, 1950); *Chem. Abstracts*, **44**, 6624 (1950).

TABLE 40

Cyanoethyl Cellulose: Relation of Sodium Hydroxide Concentration to Degree of Substitution (Somers)[225]

Viscose, ripeness, 6; mole ratio, acrylonitrile:cellulose, 1:1					
NaOH, %	6	10	15	20	25
Nitrogen, %	1.6	1.45	0.76	0.38	0.15
Cyanoethyl, D.S.	0.16	0.14	0.06	0.02	0.01
Carboxyethyl, D.S.	—	—	—	—	—
Viscose, ripeness, 8; mole ratio, acrylonitrile:cellulose, 3:1					
NaOH, %	6	20			
Nitrogen, %	—	—			
Cyanoethyl, D.S.	0.8	0.09			
Carboxyethyl, D.S.	—	0.12			

in hydrolysis that is caused by an increase in sodium hydroxide concentration.

(e) ORGANOSOLUBLE CYANOETHYL CELLULOSE[40, 42, 44]

Organosoluble cyanoethyl cellulose has been made from alkali cellulose, from regenerated cellulose, and from alkali-soluble ethers, but not from viscose. The xanthate group in the latter appears to interfere with the tris(cyanoethylglucose) structure[226] of the trisubstituted ether.

The reaction is carried out in a short time with weak sodium hydroxide and a large excess of acrylonitrile. The reaction appears heterogeneous, when agitation is insufficient or suitable solvents are lacking, but the average degree of substitution reaches 2.5 to 3.0, and the products are soluble in acetone, acrylonitrile, dimethylformamide, methyl formate, and β-ethoxypropionitrile. Fibers are spun and sheeting cast from acetone solution.

(f) CARBOXYETHYL CELLULOSE

Carboxyethyl cellulose may be prepared from activated olefins by cyanoethylation under hydrolytic conditions,[40,41,229] by the hydrolysis of cyanoethyl cellulose,[230] or by the reaction of alkali cellulose with esters of acrylic acid.[45] Either alkali-soluble or water-soluble ethers[231] may be prepared.

[229] M. M. Cruz (to American Viscose), U. S. Patent 2,577,844 (Dec. 11, 1951); *Chem. Abstracts*, **46**, 2801 (1952).

[230] W. M. Hutchinson (to Phillips Petroleum), U. S. Patent 2,481,513 (Sept. 13, 1949); *Chem. Abstracts*, **44**, 316 (1950); U. S. Patent 2,519,249 (August 13, 1950); *Chem. Abstracts*, **44**, 10319 (1950).

[231] L. H. Bock and A. L. Houk (to Rohm & Haas), Brit. Patent 562,584 (July 17, 1944); *Chem. Abstracts*, **40**, 464 (1946).

Alkali-soluble carboxyethyl cellulose is an indirect product of cyanoethylation with 0.2 to 0.5 mole of acrylonitrile per mole of cellulose in the presence of 15 to 40% NaOH for an extended time. Water-soluble carboxyethyl cellulose results when at least one mole of acrylonitrile per mole of cellulose is used.

The addition of acrylate esters to alcohols was studied by Rehberg,[232] who found that high temperatures and long times should be avoided. Esters of acrylic acid add to cellulose, but the free acid and its salts do not.[233]

$$R_{cell}OH + CH_2{=}CH_2COOR \xrightarrow{NaOH} R_{cell}OCH_2CH_2COONa + ROH \qquad (23)$$

(g) OTHER ETHERS

A mixed *O*-carbamylethyl *O*-carboxyethyl cellulose is made by the reaction of acrylamide with cellulose, followed by partial hydrolysis.[46]

Sulfoethyl cellulose has been prepared from vinylsulfonic acid,[39,47] its salts and esters; from ethionic acid, or its anhydride, carbyl sulfate.[37] Sulfamylethyl celluloses soluble in dilute alkali, but precipitated by acid, were prepared from vinylsulfonamide.[234]

Vinylamine does not exist, but its cyclic isomer, ethylenimine, reacts with viscose solutions at 100°C. to give acid-soluble products that correspond in structure to the product to be expected from vinylamine (β-aminoethyl cellulose). Ethylenimine serves as its own catalyst.[51] Cellulose diethylaminoethyl ethers were prepared by Vaughan[235] and by Grassie.[236]

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[232] C. E. Rehberg, M. B. Dixon, and C. H. Fisher, *J. Am. Chem. Soc.*, **68**, 544 (1946).

[233] V. R. Grassie (to Hercules Powder Co.), U. S. Patent 2,539,417 (Jan. 30, 1951); *Chem. Abstracts*, **45**, 4552 (1951).

[234] V. R. Grassie (to Hercules Powder Co.), U. S. Patent 2,580,351 (Dec. 22, 1951); *Chem. Abstracts*, **46**, 2802 (1952).

[235] C. L. P. Vaughan (to Hercules Powder Co.), U. S. Patent 2,591,748 (April 8, 1952); *Chem. Abstracts*, **46**, 5842 (1952); U. S. Patent 2,623,042 (Dec. 23, 1952); *Chem. Abstracts*, **47**, 3564 (1953).

[236] V. R. Grassie (to Hercules Powder Co.), U. S. Patent 2,623,041 (Dec. 23, 1952); *Chem. Abstracts*, **47**, 3564 (1953).

F. XANTHATES

EMIL KLINE[1]

When cellulose is treated with sodium hydroxide solution of mercerizing strength to form alkali cellulose (sometimes referred to as soda cellulose; see Section D of this Chapter IX) and this alkali cellulose is then treated with carbon disulfide, interaction occurs with the formation of a sodium salt of the cellulose ester of dithiocarbonic acid, more familiarly known as cellulose xanthate. The formation of this ester of cellulose is broadly represented as follows:

$$\mathrm{R_{cell}ONa + CS_2 \longrightarrow R_{cell}OCSSNa} \qquad (1)$$

This reaction, which was discovered in 1892 by Cross, Bevan, and Beadle,[2] is known as the "viscose reaction" since it is the basis of the preparation of "viscose"—a solution of the xanthate in dilute sodium hydroxide solution. (The name "viscose" originates from the viscous nature of the solution and is a condensation of *viscous cellulose.*) It is one of the most interesting reactions of cellulose and, because of low cost, industrially one of the most important. Unlike most of the other cellulose derivatives, however, the xanthate is not of interest for itself but only as a means of solubilizing cellulose, from which solution (i.e., viscose) the cellulose may be regenerated in almost any desired shape or form. The viscose process has thus found use in the production of rayon, staple fiber, cellophane, sausage casings, bottle caps, artificial sponges, sizings, and related products, and has been and still is the leading process in their manufacture. The industrial importance of the process will be appreciated when it is considered that in 1950 about 3,350,000,000 lb. of finished products,[3] valued by current U.S. standards at approximately $1,750,000,000, were produced from viscose. These products required the preparation of about 20,000,000 tons of viscose.

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[1] The author is indebted to and wishes to acknowledge the extremely valuable assistance of Gertrude M. Weisz in revising this Section.

[2] C. F. Cross, E. J. Bevan, and C. Beadle, *Ber.*, **26**, 1090 (1893); C. F. Cross and E. J. Bevan, *Ber.*, **34**, 1513 (1901); C. F. Cross, E. J. Bevan, and C. Beadle, U. S. Patent 520,770 (June 5, 1894); Brit. Patent 8700 (Feb. 6, 1893); *J. Soc. Chem. Ind.* (*London*), **12**, 516 (1893).

[3] For 1950 rayon and staple production and prices see *Rayon Organon*, **22** (June, 1951).

Since the changes in cellulose upon reaction with carbon disulfide and the regeneration of the cellulose from the viscose solution are of interest chiefly as carried out industrially in the viscose process, the xanthates will be discussed mainly from this viewpoint.

1. Preparation of Viscose

(a) SMALL-SCALE LABORATORY METHODS

The conventional procedure for the preparation of viscose involves a series of steps. Alkali cellulose is first produced by steeping cellulose in sodium hydroxide solution, pressing to remove the excess liquor, shredding, and aging to the desired viscosity. The alkali cellulose is then xanthated by reacting with carbon disulfide, and the xanthate is dissolved in dilute sodium hydroxide solution. The viscose thus produced is filtered, subjected to a vacuum treatment to remove air, and ripened to the desired point, after which it is ready for use. These operations may be carried out on a small scale as follows:

Place 100 g. (about 7 sheets, 6 in. by 6 in.) of air-dry, rayon-grade, "low-alpha" sulfite cellulose sheets (see Table 41) edgewise in a rectangular nickel tank or glass battery jar (7 in. wide by 7 in. high by 2.5 in. long) in a water bath at 21 °C. Fill the tank slowly to about 1 in. above the pulp with 18.0% NaOH solution (see Table 42), previously adjusted to 21 °C. Allow the pulp to remain in the caustic solution for 1 hr., maintaining the temperature at 21 °C. ± 0.5 °C.

Siphon or pour off the caustic. Stack the steeped sheets carefully on a perforated nickel plate and cover with another similar plate. Place the plates and the alkali cellulose in a laboratory hydraulic or hand "letter" press and press to a weight of 300 g. Shred the pressed sheets in a small Werner-Pfleiderer shredder for 2 hrs., maintaining the temperature at 21 °C. ± 0.5 °C., and then place the shredded alkali cellulose in a two-quart glass fruit jar. Seal and place the jar on mechanical rollers in a water bath at 21 °C. Allow the alkali cellulose crumbs to age for 65 hrs. under these conditions (constant rotation at 21 °C. ± 0.5 °C.).

After aging, add 32 g. of CS_2, reseal, and replace the jar on the mechanical rollers in the water bath. Allow the mass to rotate for 3 hrs. at 21 °C. ± 0.5 °C. When the reaction with CS_2 has been completed, remove the jar from the rolls, evacuate it to remove any excess CS_2, then add 169 g. of 18% sodium hydroxide solution and 764 g. of water. Stir with a mechanical agitator (nickel or stainless steel) for 2 hrs., until solution is complete, still maintaining the temperature at 21 °C. ± 0.5 °C. This will give about 1265 g. of viscose containing 7% cellulose and 6% NaOH, with a viscosity of 40 to 50 poises and a total sulfur content of about 2.0%. After adequate filtration and ripening (discussed later), the viscose will be comparable to a commercial solution and useful for the preparation of filaments, films, and the like.

As will be clear from the discussion which is to follow, exact specifications covering viscose composition, alkali cellulose aging time, and viscosity cannot be stated without identifying in detail the type of cellulose and sodium hydroxide. If the desired viscose composition and viscosity are not obtained, duplicate runs should be made in which the alkali cellulose is analyzed for per cent of cellulose and per cent of NaOH, and the alkali cellulose aging time varied. From the analysis of the alkali cellulose, the correct amounts of NaOH and water to be added to the xanthate can be calculated. By plotting the logarithm of the alkali cellulose aging time against the logarithm of the viscose viscosity for two, three, or more runs, straight-line relationships are obtained from which the exact time for any given viscosity can be determined.

If cellulose is not available in the form of sheets, viscose can be prepared from bulk pulp, or from a good grade of absorbent cotton, by carrying out the steeping operation in a beaker or any suitable vessel equipped with an agitator. The ratio of 18% NaOH solution to cellulose should be about 25 to 1. After the treatment with NaOH, the excess liquor may be removed from the bulk pulp contained in a cloth bag by centrifuging or pressing, and then proceeding as described above.

For the laboratory preparation of small amounts of viscose, a number of other procedures[4,5] may be used provided it is not required to meet commercial standards of composition, viscosity, and other specific properties. One such procedure,[6] based on an emulsion xanthation technique, is:

Mix 3.5 g. of air-dry, rayon-grade pulp with 31 ml. water for 1 hr. in a 150-ml. wide-mouthed, glass-stoppered bottle. Then add 200 mg. glucose, 3 mg. abietic acid, 50 ml. 22.5% NaOH solution, and finally 3.5 ml. CS_2. Stopper the bottle tightly, shake the contents for 15 min., and then rotate the bottle slowly for 6 hrs. at 20.0 °C. ± 0.1 °C.

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[4] R. Bartunek, *Cellulosechemie*, **22**, 56 (1944); *Das Papier*, **2**, 442 (1948); G. Jayme and coworkers, *Papier-Fabr.*, **37**, 97, 109 (1939); **38**, 93, 101, 113, 277 (1940); *Das Papier*, **1**, 133 (1947); *Svensk Papperstidn.*, **50**, 117 (1947); *Melliand Textilber.*, **28**, 125 (1947); K. Hess and coworkers, *Kolloid-Z.*, **98**, 148 (1942); *Kunstseide u. Zellwolle*, **27**, 37 (1949); O. Samuelson and coworkers, *Svensk Papperstidn.*, **51**, 331 (1948); **52**, 448 (1949); *Svensk. Kem. Tid.*, **61**, 79 (1949); R. Vuori, *Svensk Papperstidn.*, **49**, 95 (1946); Dissertation, Helsinki (1947); H. Haas, *Das Papier*, **2**, 397 (1948); T. Bergek, *Norsk Skogind.*, **2**, 289 (1948); K. Jung, *Kolloid-Z.*, **98**, 192 (1942); **108**, 120 (1944); G. Centola and F. Pancirolli, *Ind. carta* (Milan), **1**, 63, 75 (1947); J. Löbering, *Kolloid-Z.*, **98**, 186 (1942); W. Klauditz and coworkers, *Cellulosechemie*, **22**, 20, 121 (1944); W. Schramek, *Cellulosechemie*, **19**, 93 (1941); **20**, 38 (1942).

[5] G. Jayme and coworkers, *Zellwolle, Kunstseide, Seide*, **48**, 47 (1943); *Cellulosechemie*, **21**, 73 (1943); *Kolloid-Z.*, **107**, 163 (1944); **108**, 20 (1944); K. Lauer and W. Mansch, *Zellwolle u. Kunstseide*, **2**, 138 (1944); T. Kleinert and coworkers, *Kolloid-Z.*, **108**, 137, 144 (1944); *Svensk Papperstidn.*, **51**, 541 (1948); L. Skark, *Papierfabr.-Wochbl. Papierfabr.*, **75**, 146 (1947); *Das Papier*, **2**, 3, 186 (1948); H. Koch, *Papier-Fabr.*, **39**, 46 (1941); W. Winkler, *Kunstseide u. Zellwolle*, **28**, 153 (1950).

[6] G. Jayme and J. Wellm, *Kolloid-Z.*, **107**, 163 (1944).

(b) LARGE-SCALE MANUFACTURE [7]

(1) *Raw Materials*

The principal raw materials entering into the manufacture of viscose are cellulose, sodium hydroxide, and carbon disulfide. Of these, cellulose is the most important because it also constitutes the end product of the process. At the present time the only practical sources of cellulose are cotton and wood. Other possible cellulosic materials[8] (agricultural residues including straw, bagasse, and cornstalks) are satisfactory, but, except in a few countries, they have been too expensive to refine to the point required by the process. When cotton is the source of cellulose, it is obtained mainly from second-cut linters and hull fiber (see Chapter VI-B). Wood cellulose (from which by far the greatest part of the world's output of viscose products is produced) is derived chiefly from softwoods such as spruce, western hemlock, and southern pine, although very satisfactory pulps are also being produced from certain of the hardwoods, including beech, aspen, and gum.[9] Actually, the kind of wood is secondary in importance to the methods used to isolate and purify the cellulose (see Chapter VI-A). For this purpose the sulfite process has been employed almost exclusively, but recent developments in the sulfate process, involving prehydrolysis, now make its use also possible for dissolving pulps.[9]

The factors which generally determine the type of cellulose to be used in the manufacture of viscose are the type of product to be produced (rayon, cellophane, staple, etc.), the quality of product, the price, and alkali cellulose aging facilities. When strength, durability, and toughness are the prime considerations (such as in the manufacture of high-tenacity rayon, sausage casings, and bottle caps), pulps high in alpha-cellulose content, including those from cotton linters, and with uniform chain length, minimum impurities, and a minimum quantity of cellulose with degree of polymerization (D.P.) less than about 150, are necessary, or at least are desirable.[10] When these requirements are not quite so important, or when price is a deciding factor, pulps lower in alpha-cellulose content and poorer in color are used. Although most pulps are produced in what might be described as a "medium" or "normal" range of viscosity, "low-viscosity" pulps are also in use; the latter require only one-half to one-third the aging time of the normal-viscosity pulps.

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[7] V. Hottenroth, *Artificial Silk*, Pitman, London, 1928; E. Wheeler, *The Manufacture of Artificial Silk*, Van Nostrand, New York, 1931; M. H. Avram, *The Rayon Industry*, Van Nostrand, New York, 1929; O. Faust, *Kolloidchem. Tech.*, No. 2, 124 (1931); W. Weltzien and K. Götze, *Chemische und Physikalische Technologie der Kunstseiden*, Akadem. Verlagsgesellschaft, Leipzig, 1930; H. G. Bodenbender, *Zellwolle*, 2d. ed., Chemisch-technischer Verlag Dr. Bodenbender, Berlin, 1937; K. Götze, *Chemiefasern nach dem Viskoseverfahren* (*Reyon und Zellwolle*), Springer, Berlin, 1951; L. H. Smith, editor, *Synthetic Fiber Developments in Germany*, Textile Research Institute, New York, 1946; H. W. Rose, *Rayon Industry of Japan*, Textile Research Institute, New York, 1946; *Continuous and Staple Fiber Plants of Germany*, PB Rept. 377, 1945.

[8] H. Jentgen, *Kunstseide u. Zellwolle*, **24**, 350 (1942); H. Levinstein, *Chemistry & Industry*, **1948**, 538; M. G. Karnik and D. L. Sen, *J. Sci. Ind. Research* (*India*), **7**, 351 (1948); **9B**, 201 (1950).

[9] S. Wang, *Rayon and Melliand Textile Monthly*, **15**, 227 (1934); J. N. McGovern and G. K. Dickerman, *Paper Trade J.*, **124**, 33 (Jan. 9, 1947); L. L. Leach, *Rayon Textile Monthly*, **26**, 631 (1945); *Chem. Inds.*, **67**, 576 (1950).

The various types of acceptable commercial pulps on the market at the present time may be divided into five groups according to a combination of alpha-cellulose content, cuprammonium viscosity, and principal end use. The normal ranges of the common analytical characteristics of the pulps in each of these groups are given in Table 41.[11]

It should be understood that, although analytical characteristics as shown in Table 41 are of prime importance, a chemical analysis alone of a pulp is not sufficient to establish its value as a source of cellulose for viscose. As a matter of fact, exact specifications covering the cellulose raw material cannot be set up since complete information is still lacking to correlate all of the various characteristics of a pulp with the process and end product. In addition to having a satisfactory chemical analysis, the pulp must be sufficiently reactive to NaOH and CS_2 to give a good solution (good-filtering viscose), and it must always be uniform in all respects, including reactivity, chemical analysis, viscosity, D.P. distribution, color, and sheet structure.[4] In this connection, considerable attention has been given by a number of investigators to the influence of various pulp properties and characteristics, and several test procedures for evaluating pulps as to their suitability for viscose have been proposed.[4,5] Some of these

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[10] O. P. Golova, *Kunstseide*, **17**, 302 (1935); E. Lindpaintner, *Melliand Textilber.*, **23**, 229, 281 (1942); A. LeRollan, *Ind. textile*, **62**, 144 (1945); O. Samuelson, *Svensk. Kem. Tid.*, **59**, 105 (1947); R. Bartunek, *Das Papier*, **4**, 451 (1950); E. A. Tippetts, *Tappi*, **33**, 32 (1950).

[11] A. Waller, *Thé Svedberg* (Memorial Volume), **1944**, 400; A. H. Hooker and coworkers, U. S. Patent 2,079,120 (May 4, 1937); *Chem. Abstracts*, **31**, 4495 (1937); F. E. Bartell and H. Cowling, *Ind. Eng. Chem.*, **34**, 607 (1942); R. L. Mitchell, *Ind. Eng. Chem.* **43**, 1786 (1951); U. S. Patent 2,542,285 (Feb. 20, 1951); *Chem. Abstracts*, **45**, 4042 (1951). For changes in some of the basic analytical characteristics of pulps due to various viscose processing operations see: A. Pakschver and coworkers, *Trans. Inst. Chem. Technol. Ivanovo* (*U. S. S. R.*), **3**, 158 (1940); A. Riedemann, *Rayon Textile Monthly*, **29**, No. 8, 45, No. 9, 82 (1948); R. L. Mitchell, *Ind. Eng. Chem.*, **41**, 2197 (1949).

TABLE 41

Analytical Characteristics of Commercial Viscose Pulps[a]

Unpublished data compiled from analyses by pulp vendors

Group	Low-alpha wood pulps		High-alpha wood pulps		Cotton linters pulps
	Normal viscosity	Low viscosity	Normal viscosity	Low viscosity	
Principal end use	Textile rayon	Cellophane	Tire cord	Tire cord	Tire cord and film
% Alpha-cellulose	89.0 –92.0	87.0 –91.0	94.0 –96.0	93.5 –95.5	98.0 –99.0
% Beta-cellulose	3.0 – 5.0	5.0 – 7.0	2.0 – 3.0	2.0 – 3.0	1.0 – 1.5
% Gamma-cellulose	3.0 – 6.0	3.0 – 5.0	1.5 – 3.5	2.0 – 4.0	0.0 – 1.0
% 10% KOH-soluble	10.0 –17.0	13.0 –20.0	6.0 –10.0	6.0 –10.0	1.5 – 4.0
% Ether extract	0.1 – 0.3	0.1 – 0.3	0.05 – 0.15	0.02 – 0.10	0.05– 0.10
% Ash	0.04 – 0.13	0.05 – 0.13	0.04 – 0.08	0.04 – 0.08	0.05– 0.10
% Silica	0.005– 0.02	0.003– 0.02	0.004– 0.02	0.004– 0.02	0.01– 0.15
% Calcium	0.01 – 0.05	0.01 – 0.05	0.01 – 0.03	0.01 – 0.03	0.01– 0.03
Iron, p.p.m.	5–15	5–15	5–15	10–20	10–25
Cuprammonium viscosity, (ACS method, cps.)	250–700	100–200	250–700	75–175	250–350

[a] In addition to the above analytical characteristics, the amounts of other metallic impurities such as copper, manganese, nickel, and aluminum, and of other organic impurities associated with cellulose, such as lignin and pentosans, are also of importance and should be uniform and as low as possible. Since viscose viscosity does not always parallel cuprammonium viscosity, the viscosity figures do not necessarily reflect directly the alkali cellulose aging times required for the various pulps.

involve the determination of D.P. distribution, end groups, total hydrolyzates, and similar properties. Many involve the preparation of viscoses of special compositions and the examination of these viscoses for particular characteristics such as filterability, unfiltered residues, and mercerization resistance. These procedures are undoubtedly useful in establishing approximate values. However, the only way to reach a final conclusion regarding the utility of a given type of cellulose is actually to convert it into commercial-type viscose and into the particular end product (filaments, films, etc.) desired.[12]

The principal considerations in connection with the water and caustic soda used in the viscose process are the impurities which may be present, mostly metallic salts,[11] which affect the viscosity, color, and solubility of the xanthate and certain characteristics of the final product. It is important that all metallic and other impurities be uniform and as low as possible in concentration. The water also should be soft, preferably of zero hardness. In caustic soda, the impurities vary somewhat depending upon the type (caustic liquor versus solid caustic and ammonia–soda process versus electrolytic process), although most producers have now so refined their operations and so reduced all impurities that there is relatively little variation in chemical analysis from one producer's material to another. Caustic is usually supplied in the form of 50% liquor, in specially lined tank cars; some 73% liquor is also made for viscose. Solid caustic, which was employed almost universally some years ago, still finds some use, particularly where caustic must be transported over long distances. The range of impurities usually found in 50% caustic liquor used for viscose is shown in Table 42.

TABLE 42

Representative Analysis of a 50% Caustic Liquor

Unpublished data compiled from analyses by du Pont Co. and by caustic vendors

Material	%	Material	P.p.m.
		Fe	3–6
NaOH	50.0 –50.5	Ca	1–15
Na_2SO_4	0.001– 0.08	Al	10–20
Na_2CO_3	0.05 – 0.20	Mg	5–15
NaCl	0.05 – 0.20	Mn	0.3–0.5
SiO_2	0.005– 0.02	Cu	0.3–0.6
		Ni	0.0–0.5

[12] C. H. Goldsmith, *Rayon and Melliand Textile Monthly,* 16, 513 (1935); K. Fabel, *Kunstseide,* **17,** 42 (1935).

The carbon disulfide used for viscose is essentially a chemically pure product made usually by the direct interaction of carbon and sulfur under definite conditions. For this reason there is usually no need for concern over specifications, even though impurities, particularly free sulfur, should be absent for optimum xanthate solubility.

(2) *Preparation of Alkali Cellulose*

(*a*) *Steeping.* The first step in the viscose process, as indicated above, is the treatment of the cellulose raw material with sodium hydroxide solution of mercerizing strength. This treatment, known as the steeping operation, has two specific and distinct objectives: (1) swelling and absorption of NaOH with the uniform and complete formation of alkali cellulose I, and (2) the removal of hemicellulose and other impurities from the cellulose.

In conventional industrial operation, the cellulose raw material (pulp), in the form of sheets, is placed edgewise in a steeping press, that is, a rectangular tank, with a ram at one end actuated by a screw or hydraulic pressure. The size of the press charge varies considerably. In the United States, batches of 100 to 600 lb. are normal, the sheets varying from about 13 in. by 18 in. to 20 in. by 27 in. In Europe, charges as large as 2000 lb.[13] are said to be in use, with sheet sizes up to 30 in. by 40 in. The press is filled slowly with caustic solution containing about 18% NaOH and 0.5 to 3.0% hemicellulose; then the reaction is allowed to proceed for 30 to 60 min. at a definite temperature, the normal range being 15–35°C. (The reaction being exothermic, a rise in temperature of 2–3°C. usually occurs.)

Of the factors that control the steeping operation, the nature of the pulp,[4,5] the time, the temperature, and the concentration of NaOH[14] are all-important. For the formation of alkali cellulose I the concentration of NaOH must lie in the region in which alkali cellulose I is stable, that is, about 14 to 20% NaOH. When the operation is carried out in a conventional steeping press, 18% NaOH usually gives about the best results from the viewpoint of xanthation efficiency and viscose filterability (see Fig. 71).[15] Deviations from this concentration of the order of ±1 to 2% may not be particularly harmful if suitable adjustments are made, but neither are they advantageous except in specific instances. Swelling of the pulp varies with NaOH concentration; the lower the concentration (to about

[13] H. Jentgen, *Kunstseide*, **18**, 408 (1936).

[14] A. Breguet and coworkers, *Mém. services chim. état* (*Paris*), **34**, 157 (1948).

[15] The data in Figures 71–74, inclusive, are representative of a typical commercial viscose containing 7.5% cellulose and 6.5% NaOH, made from a 95% alpha-cellulose pulp, pressed, after steeping, to a press weight ratio of 2.6 to 1.0 and xanthated, unless otherwise indicated, with 34% CS_2 based on the cellulose in the alkali cellulose.

9%), the higher is the swelling. The NaOH concentration also affects the composition and the rate of aging of the alkali cellulose; the higher the concentration of the NaOH, the faster is the aging.

Temperature is important in steeping mainly because of its effect on swelling, which decreases with increasing temperature. Higher temperatures therefore result, for example, in lower hemicellulose losses, higher yield, stronger steeped sheets, less slumping in the press, and easier pressing. Lower temperatures, on the other hand, by increasing swelling, result in greater pulp reactivity and in increased absorption of caustic. From these effects, it will be obvious that steeping temperature also is a factor in determining viscose viscosity, viscose ripening, and alkali cellulose composition.

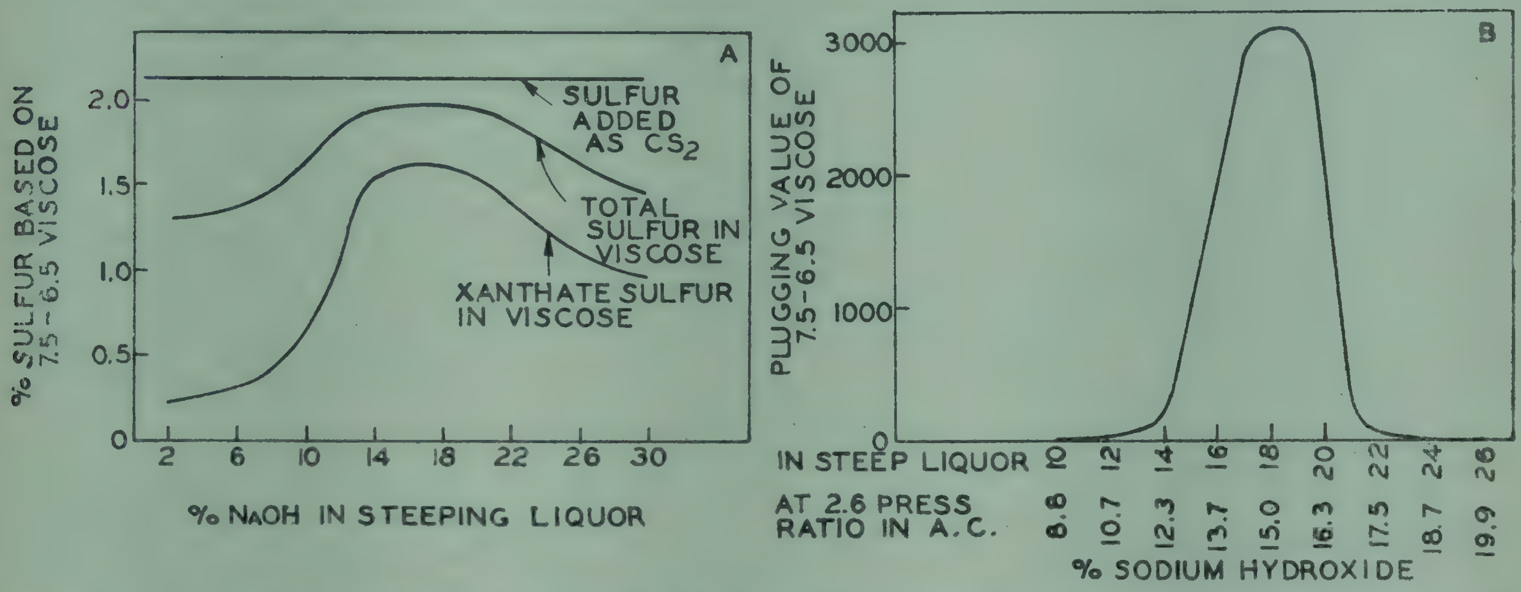

Fig. 71. Effect of NaOH content of steep liquor and alkali cellulose (A. C.) on viscose characteristics[15]: (A) effect on CS_2 absorption and distribution; (B) effect on filterability (plugging value). Courtesy of Research Division, Rayonier Incorporated.

Since mercerization is a relatively rapid reaction, time of steeping is determined largely by the time necessary to solubilize and remove the hemicellulose and other impurities from the pulp. As much as 15 min. is required to remove the main portion of hemicelluloses from some pulps in a conventional steeping press, hence this may be considered about the minimum permissible time. Additional time is desirable, especially with large sheets, and 30 to 60 min. (in some instances 2 hrs.) is usually employed.

Some of the other variables[16] which affect the conventional steeping operation are type and concentration of hemicellulose, pulp sheet density (the number of sheets per inch in the press), rate of filling of the steeping press, pulp sheet formation and structure, and use of wetting agents.

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[16] *Steeping Procedure*, Rayonier Incorporated, San Francisco, April, 1941; E. Ringström and N. H. Apler, *Svensk Papperstidn.*, **51**, 501 (1948).

The amount of hemicellulose present influences the uniformity of mercerization, the rate of alkali cellulose aging and xanthation, the solubility of the xanthate, the rate of viscose ripening, and the characteristics of the final product. It is desirable that the hemicellulose content of the steeping solution be kept low. It is not economically feasible, however, to discard the caustic used in the operation; hence, it is almost universal practice to return it to the process and to remove the hemicellulose from a portion of the solution by dialysis, thus maintaining a constant, fairly low concentration of hemicellulose in the steeping liquor. Although it has been proposed to add to the steeping solution various other materials, including wetting agents (which improve caustic penetration and shredding, thus giving more uniform xanthation and improved solution), sodium sulfide, metallic salts, and oxidizing agents (for reducing viscosity),[17] alcohols, proteins, and starch, few, if any, of these have found practical use.

(*b*) *Pressing.* Since sodium hydroxide reacts with carbon disulfide to form useless by-products (see below), it is desirable to remove most, but not all, of the excess NaOH from the alkali cellulose before this reaction. For this reason, after steeping, the solution is drained from the tank and the steeped pulp is pressed to about three times the weight of the original air-dry pulp. As indicated, the waste solution, containing the hemicellulose removed from the pulp, is dialyzed and used over again.

The ease of pressing is inversely proportional to the degree of swelling and, hence, is determined by type of pulp, temperature, and concentration of NaOH. The pressing factor or press–weight ratio (ratio of weight of pressed alkali cellulose to original air-dry pulp) controls the composition of the alkali cellulose as well as of the waste caustic solution. With an ordinary rayon-grade pulp (91% alpha-cellulose) and 18% NaOH solution, a press–weight ratio of 3.0 to 1.0 gives an alkali cellulose containing approximately 29.8% cellulose, 15.2% NaOH, and 55% H_2O. Changing the press–weight ratio changes the cellulose content, the NaOH content remaining nearly constant. At a press–weight ratio of 2.5 to 1.0, for example, the analysis is about 35% cellulose, 15% NaOH, and 50% H_2O. For further details as to the effect of pressing and other variables on the composition of the alkali cellulose, see Section D of this Chapter IX.

The press–weight ratio also influences shredding, the rate, efficiency, and uniformity of xanthation, the rate of degradation of the cellulose during alkali cellulose aging, and the properties of the final product. The lower the ratio is, the poorer is the shredding and the slower is the alkali cellulose aging and the rate of carbon disulfide absorption. However, xanthation is more efficient at the lower ratios, and solubility is improved, provided shredding is satisfactory. In commercial operation, the pressing factors employed are in an intermediate range from 2.7–1.0 to 3.2–1.0, which represents a compromise between poor shredding and low reaction rate on the one hand and gelatinization of the fibers on the other.

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[17] For example, see A. H. Hooker and coworkers, U. S. Patent 2,079,120 (May 4, 1937); *Chem. Abstracts*, **31**, 4495 (1937); D. Entwistle and W. R. Weigham, U. S. Patent 2,542,492 (Feb. 20, 1951); *Chem. Abstracts*, **45**, 4454 (1951).

(*c*) *Shredding*. After removal of the excess caustic by pressing, the alkali cellulose is mechanically disintegrated or shredded for 1 to 3 hrs. at 25° to 35°C. to form a mass of fibers resembling bread crumbs. This serves to increase the surface of the alkali cellulose and to insure rapid and uniform aging and xanthation. To achieve further uniformity and low cost, two or more steeping press charges may be combined into a single shredder charge. The operation is conventionally carried out in equipment resembling a dough mixer, that is, a Werner-Pfleiderer shredder, which tears the sheets between rapidly rotating blades and a stationary saddle.

Optimum shredding is indicated by a maximum of fibrillation without agglomeration or knot formation. Although various tests, such as determination of particle size and density, have been devised for evaluating shredding, none are really significant. In addition to the factors already mentioned, time and temperature[18] must be carefully controlled, not only to secure optimum shredding, but also to control the oxygen absorption and hence degradation of the cellulose which always occur during this stage.

(*d*) *Aging*. After the shredding operation, the alkali cellulose crumbs, in cylindrical or rectangular steel containers (usually one container per shredder batch), are placed in a constant-temperature room for 1 to 3 days at 25° to 30°C.; this step in the process is called "aging." In some cases, however, the aging step has been simplified and/or shortened by the use of low-viscosity pulps, aging before shredding, high-temperature shredding, continuous aging, and other means. The crumbs are kept carefully covered to prevent reaction with CO_2 from the air and evaporation of moisture which would be detrimental to xanthation and filterability. During this step (see Section D of this Chapter IX) further absorption of oxygen occurs with generation of heat, and the viscosity of the cellulose is reduced. This reduction in viscosity is essential since the solution viscosities which would otherwise be obtained from present-day, unaged, commercial celluloses would be considerably higher than desired. The rate and extent of the viscosity reduction during aging are controlled by temperature and time[19]; the higher the temperature, the faster is the aging (the temperature coefficient is high), and the longer the time, the lower is the viscosity. Other factors influencing aging[11,20] include type of cellulose and caustic soda, presence of oxidizing agents or metallic impurities such as iron and manganese which accelerate the reaction, xanthation conditions, and viscose composition.

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[18] M. Huzii, *J. Soc. Chem. Ind., Japan*, **43,** Suppl. binding, 191 (1940).

(3) *Xanthation of Alkali Cellulose*

The xanthation of alkali cellulose is the most significant step in the making of viscose, since here the actual conversion of the cellulose to a soluble derivative takes place. For this purpose, the aged alkali cellulose is usually placed in a hexagonal or cylindrical rotating drum or a "wet churn,"[21] and CS_2 is slowly admitted as a gas or liquid through a perforated pipe within the drum. The reaction is permitted to continue for 1 to 3 hrs., in the temperature range 20–35°C., either at atmospheric pressure or under vacuum. The quantity of CS_2 added is usually between 30 and 40%, based on the cellulose in the alkali cellulose. As the reaction proceeds, the white alkali cellulose gradually becomes yellow and finally assumes an orange or "carrot" color. The end product usually retains some of its original crumbly, mealy character although it is somewhat sticky; its actual color and physical characteristics are determined in part by the alkali cellulose composition, the CS_2 concentration, and the temperature and time of reaction.

Several of the factors influencing the xanthation reaction have been mentioned. It may be added that (1) the nature (e.g., type morphology, and purification) of the cellulose[4,5] affects the rate and degree of xanthation and the amount of CS_2 required to produce good solubility; (2) the degree of xanthation increases and solubility improves with increasing concentration of CS_2 but both reach a maximum beyond which further amounts of CS_2 have little, if any, effect; (3) the uniformity of CS_2 distribution is important for good solubility (crowding the xanthation vessel, for example, affects filtration adversely); (4) the rate of xanthation, which reaches a maximum and then falls off, is probably independent of the D.P. of the cellulose but is proportional to the vapor pressure of the CS_2 and the temperature; (5) the maximum degree of xanthate substitution decreases with increase in temperature, but solubility increases with increase in temperature in the range 15–35°C., the time and CS_2 concentration being constant; if the time is reduced accordingly, solubility decreases above about 30°C.; (6) the time of reaction, which may be measured by the time to re-establish the original xanthation pressure, increases with CS_2 concentration; it should be sufficient for complete absorption of CS_2, but the degree of xanthation does not increase nor does the solubility improve with further reaction time; (7) the solution viscosity of the cellulose is markedly reduced by oxidation during xanthation, hence temperature and presence of oxygen are important factors; (8) the stability of the xanthate decreases with increase in temperature, increase in press–weight ratio, increase in degree of xanthation, and increase in hemicellulose content; and (9) xanthation conditions, particularly temperature, CS_2 concentration, and degree of xanthation, influence regeneration and the characteristics of the final product.[4,5,22] For the effect of a number of xanthation conditions on xanthation rate, CS_2 absorption, and solubility (viscose filterability), see Figures 72 and 73.

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[19] A. V. Pitter, *J. Soc. Dyers Colourists*, **51**, 21 (1935).

[20] I. Jurisch, *Kunstseide u. Zellwolle*, **23**, 266 (1941); O. Samuelson, *Cellulosa och Papper 1908–1948*, S.P.C.I., pp. 295–325; G. A. Schröter, *Kolloid-Z.*, **105**, 223 (1943).

[21] M. Golben, U. S. Patent 2,492,421 (Dec. 27, 1949); *Chem. Abstracts*, **44**, 2240 (1950); E. Kline, U. S. Patent 2,513,652 (July 4, 1950); *Chem. Abstracts*, **44**, 8658 (1950).

At the end of the xanthation reaction the excess CS_2 is removed by evacuation, and the mass is dissolved in dilute NaOH solution to form the final solution—viscose. To achieve greater uniformity, two batches of xanthate (four steeping press charges) are often combined at this point to form a single charge. The amounts of NaOH and water employed in preparing the final solution depend upon the alkali cellulose analysis and the viscose composition (% cellulose and % NaOH) desired. The latter varies with different producers and with the type of end product, although the concentrations are usually in the range of 6.0 to 10.0% cellulose and 4.0 to 8.0% NaOH. For example, with an alkali cellulose containing 29.8% cellulose and 15.2% NaOH, a press–weight ratio of 3 to 1, 35% CS_2, and the combination of four steeping press charges of 150 lb. of pulp each, the production of a viscose solution containing 7% cellulose and 6% NaOH would require 5490 lb. of water and 186 lb. of 100% NaOH, and the total viscose weight obtained would be about 7650 lb.

Dissolving of the xanthate is referred to as the "mixing" step from the fact that it is carried out by simply mixing the xanthate and NaOH solution in a large cylindrical tank (Vissolver) equipped with an agitator. The mixing operation normally requires from 2 to 6 hrs., the temperature being controlled in the range 15–20°C.

[22] P. C. Scherer and coworkers, *Rayon Textile Monthly*, **19**, 478, 541 (1938); **20**, 24, 81, 498, 577 (1939); **21**, 529, 611 (1940); W. Schramek and E. Zehmisch, *Kolloid-Beihefte*, **48**, 93 (1938).

(4) *Ripening of Viscose*

As initially prepared, viscose is relatively difficult to coagulate and, hence, is not suitable for most industrial operations. To make it fit for applications such as spinning and casting, the viscose is transferred (usually after further blending) to large tanks in another constant-temperature room where it is stored under controlled conditions of time and temperature to permit "ripening." During this period various changes occur, the most important being spontaneous decomposition of the xanthate and an increase in ease of coagulation of the solution. However, since these changes continue until coagulation and regeneration of the cellulose are complete, the viscose cannot be stored indefinitely but must be used within a few days after preparation.

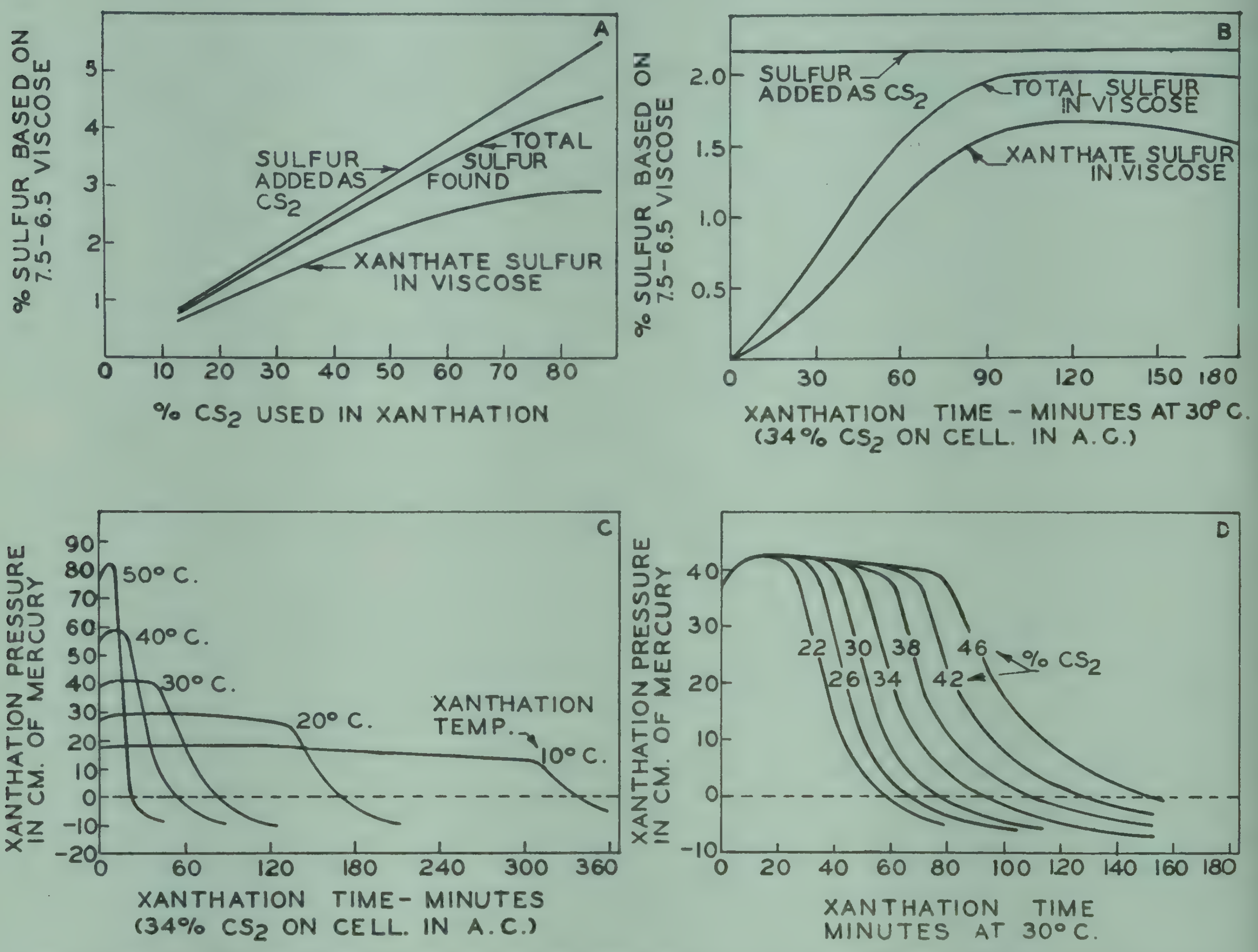

Fig. 72. Effect of certain xanthation conditions on xanthation rate and sulfur distribution[15]: (A and B) effect of (A) CS_2 concentration and (B) xanthation time on CS_2 absorption and distribution; (C and D) effect of (C) temperature and CS_2 pressure and (D) CS_2 concentration on rate of xanthation. A. C. stands for alkali cellulose. Courtesy of Research Division, Rayonier Incorporated.

For any given viscose, the rate at which ripening occurs is governed by temperature; the higher the temperature, the faster is the ripening. (Ripening is an exothermic process and the temperature coefficient of the chemical reactions involved is of the order of 2.5–3.0 per 10°C.) The extent of the ripening (and hence time) is determined (empirically) by the regenerating conditions to be used and by the use to which the viscose is to be put, that is, whether it is to be spun into threads, cast into films, or used for some other purpose. Coagulating methods have been developed in recent years which permit the use of relatively "unripe" or "green" viscose, but in most operations ripening requires 1 to 3 days, the normal temperature range being 15–25°C.

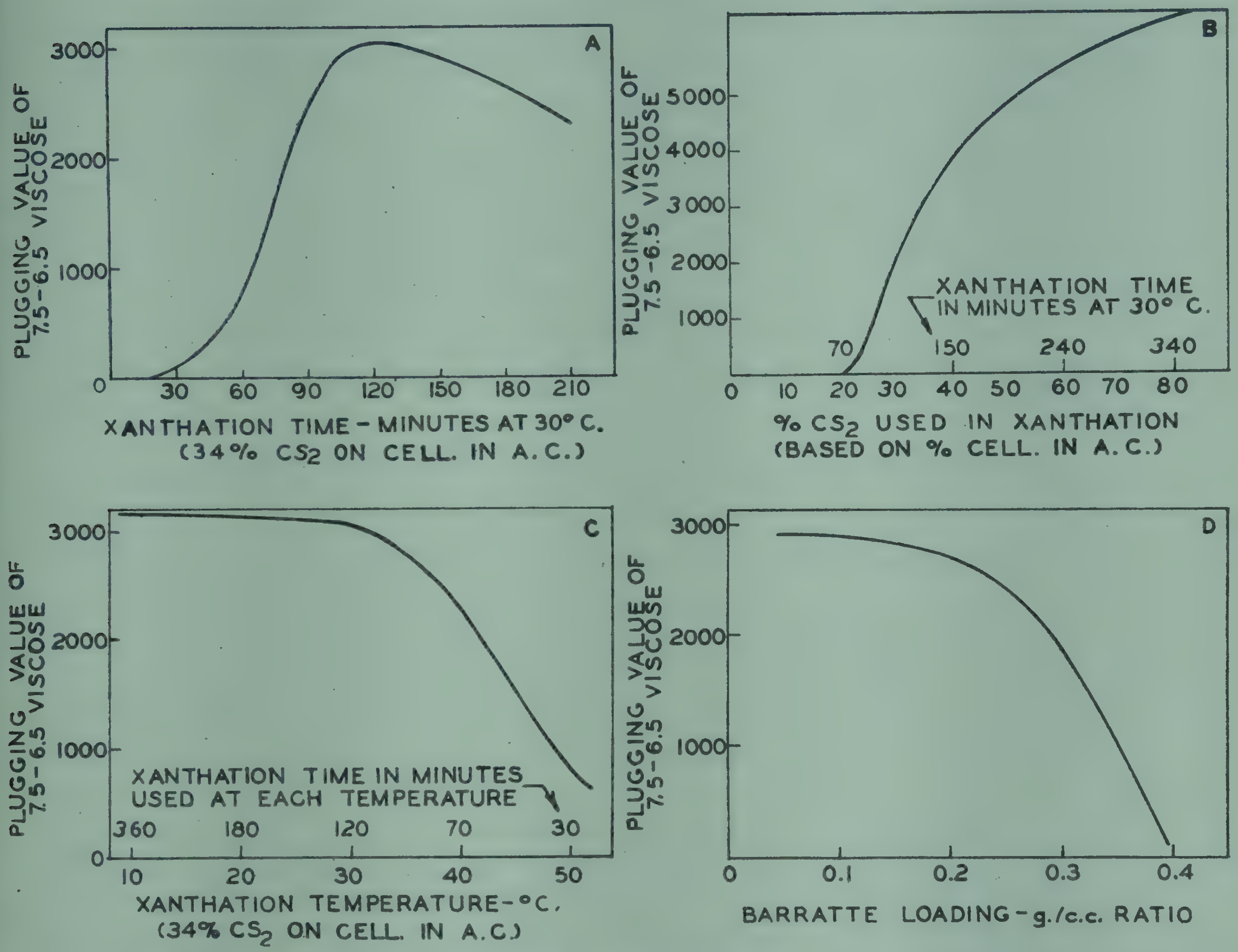

Fig. 73. Effect of certain xanthation conditions on viscose filterability (plugging value):[15] (A) effect of xanthation time; (B) effect of CS_2 concentration; (C) effect of xanthation temperature; (D) effect of Barratte crowding. A. C. stands for alkali cellulose. Courtesy of Research Division, Rayonier Incorporated.

During this period, various analyses also are carried out, the viscose is filtered (usually in two or more stages through plate and frame filter presses dressed with various combinations and types of cotton fabric and cotton batting), and finally evacuated, to remove air. When the ripening has reached the point required for conversion to the particular end product desired, the viscose is ready for use.

(c) CONTINUOUS AND "QUICK" PROCESSES

Other methods for preparing viscose, and particularly alkali cellulose, have come into use, or have been suggested, which are cheaper or which overcome some of the objections to the multistage operation just described. These mostly involve continuous methods of operation (except for the xanthation step, which apparently is not yet being carried out continuously on an industrial scale) or a reduction in the number of stages. In certain operations, pulp is treated in bulk form in tanks equipped with suitable agitators (slurry steeping), and the excess caustic is removed by vacuum filtration, centrifuging, and/or suitably designed presses or press rolls. This type of procedure, starting with either sheets or bulk pulp, may also be carried out continuously. Another continuous-type procedure involves the passing of pulp in sheets or in roll form on a conveyor through a caustic solution, followed in some cases by continuous pressing, shredding, and aging. If the viscose plant is erected adjacent to the pulp plant, the pulp may be employed without drying. Some of the other variations involve countercurrent steeping, spraying the pulp with caustic in a shredder, continuous shredding, continuous and/or quick alkali cellulose aging by use of elevated temperatures or addition of oxidizing or other agents, combination of xanthation and mixing in a "xanthator–mixer," treatment with carbon disulfide in the presence of an inert organic solvent or at extremely low temperatures, and continuous mixing by various disintegrating devices.[13,23]

[23] H. Jentgen, *Kunstseide u. Zellwolle*, **20**, 449 (1938); R. Monterray, *Rusta-Rayonne*, **13**, 517 (1938); *Rayon Textile Monthly*, **18**, 227 (1937); H. Schmidt, *Chem. Fabrik.*, **4**, 73, 85, 97 (1931); F. Steimmig, U. S. Patent 2,005,811 (June 25, 1935); *Chem. Abstracts*, **29**, 5653 (1935); German Patent 604,015 (Oct. 17, 1934); *Chem. Abstracts*, **29**, 926 (1935); French Patent 751,617 (Feb. 27, 1933); *Chem. Abstracts*, **28**, 893 (1934); H. von Kohorn zu Kornegg, U. S. Patent 2,218,836 (Oct. 22, 1940); *Chem. Abstracts*, **35**, 1227 (1941); G. A. Richter, U. S. Patent 1,955,092 (Apr. 17, 1934); *Chem. Abstracts*, **28**, 4229 (1934); L. Lilienfeld, U. S. Patent 1,658,607 (Feb. 7, 1928); *Chem. Abstracts*, **22**, 1237 (1928); H. Plauson, Brit. Patent 184,533 (April 11, 1911); *Chem. Abstracts*, **7**, 412 (1913); A. J. Hailwood, Brit. Patent 281,117 (Nov. 30, 1926); *Chem. Abstracts*, **22**, 3528 (1928); I. G. Farbenindustrie Akt.-Ges., Brit. Patent 434,540 (Sept. 4, 1935); E. I. du Pont de Nemours & Co., Brit. Patent 463,056 (Mar. 19, 1937); *Chem. Abstracts*, **31**, 6003 (1937); Deutsche Gasglühlicht-Auer-Gesellschaft m.b.H., German Patent 413,511 (Oct. 1, 1921); *Chem. Zentr.*, **96, II**, 368 (1925); W. Grötzinger, French Patent 823,836 (Jan. 27, 1938); *Chem. Abstracts*, **32**, 6058 (1938); L. H. Smith, editor, *Synthetic Fiber Developments in Germany*, Textile Research Institute, New York, 1946; H. W.

Continued on next page.

2. Mechanism of Cellulose Xanthate and Viscose Formation

On the basis of the analogy between cellulose and ordinary alcohols, the reaction between alkali cellulose and CS_2 was first represented in a manner similar to the reaction between CS_2 and alcohols in the presence of alkali. It has been known for a long time that when ethyl alcohol is treated with CS_2 in the presence of NaOH, sodium ethyl xanthate is formed, the reaction being as follows:

$$C_2H_5OH + NaOH + CS_2 \longrightarrow C_2H_5OCSSNa + H_2O \qquad (2)$$

An alcoholate is supposedly first formed by the action of the metal hydroxide on the alcohol, and then the metal xanthate is produced by the reaction of CS_2 with the alcoholate.[24] Similar compounds are formed with other metal hydroxides and other alcohols, including polyhydric alcohols and simple sugars.[25] If cellulose is substituted for the ethyl alcohol in equation 2, the analogous reaction product is sodium cellulose xanthate[26] as shown in equation 1.

Equation 2, however, may be considered only as a simple, general expression of the viscose reaction. The actual reaction is of a colloidal na-

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Rose, *Rayon Industry of Japan*, Textile Research Institute, New York, 1946; H. Hoffman, *Kunstseide u. Zellwolle*, **26**, 8 (1948); H. Von Kohorn, U. S. Patent 2,302,077 (Nov. 17, 1942); *Chem. Abstracts*, **37**, 2193 (1943); R. W. Nash, U. S. Patent 2,338,196 (Jan. 4, 1944); *Chem. Abstracts*, **38**, 3840 (1944); O. Kohorn and R. Brandes, Brit. Patent 433,414 (Aug. 14, 1935); D. Entwistle and W. R. Weigham, U. S. Patent 2,542,492 (Feb. 20, 1951); *Chem. Abstracts*, **45**, 4454 (1951); N. A. Copeland, U. S. Patent 2,355,057 (Aug. 8, 1944); *Chem. Abstracts*, **38**, 6561 (1944); J. P. Hollihan, Jr., U. S. Patent 2,355,650 (Aug. 15, 1944); *Chem. Abstracts*, **39**, 192 (1945); W. R. Schmitz, Jr., U. S. Patents 2,360,984 (Oct. 24, 1944); 2,364,392 (Dec. 5, 1944); *Chem. Abstracts*, **39**, 3666 (1945); W. H. Bradshaw, U. S. Patent 2,452,542 (Nov. 2, 1948); *Chem. Abstracts*, **43**, 2435 (1949); J. Brackett, U. S. Patent 2,480,998 (Sept. 6, 1949); *Chem. Abstracts*, **44**, 1705 (1950); J. G. Weeldenberg, U. S. Patent 2,499,010 (Feb. 28, 1950); *Chem. Abstracts*, **44**, 4678 (1950); M. P. Kulp, U. S. Patents 2,510,984 (June 13, 1950); *Chem. Abstracts*, **44**, 8658 (1950); 2,539,437 (Jan. 30, 1951); *Chem. Abstracts*, **45**, 3598 (1951); Suddeutsche Zellwolle A.G., Belgian Patent 450,505 (June, 1943); *Chem. Abstracts*, **41**, 7118 (1947).

[24] K. Atsuki and T. Takata, *Cellulose Ind.* (Tokyo), **16**, 21 (1940); but see also A. E. Brodsky and coworkers, *J. Chem. Phys.*, **11**, 342 (1943); I. A. Makolkin, *Acta Physicochim.* (*U. R. S. S.*), **17**, 319 (1942).

[25] M. Ragg, *Chem. Ztg.*, **34**, 82 (1910); E. Berl and J. Bitter, *Cellulosechemie*, **7**, 137 (1926); T. Lieser and coworkers, *Ann.*, **495**, 235 (1932); **511**, 121 (1934); E. Treiber, *Monatsh.*, **82**, 53 (1951).

[26] The name xanthate is derived from the Greek word "xanthos," meaning yellow, in view of the yellow color of the cuprous salt of xanthic acid. It should be mentioned also that xanthic acid is really the ethyl ester of dithiocarbonic acid and therefore the term cellulose xanthate is a misnomer. The latter compound is not the cellulose ester of xanthic acid but of unsymmetrical dithiocarbonic acid.

ture and is far more complicated. It has been the subject of numerous investigations,[2,4,5,22,27] the more important of which will be discussed below. These have now answered many of the questions concerning the mechanics and chemistry involved, although a number of the conclusions that have been reached are even now not universally recognized and further study of the reaction is still needed for its complete understanding. Progress in the field has been difficult due to the chemical instability of the xanthate and even more to the prevalence of questionable conceptions about the nature of cellulose reactions and the properties of high-polymer solutions.

Unlike many of the other cellulose derivatives such as the trinitrate and triacetate, the trixanthate does not form readily. In the commercial viscose reaction, for example, the average degree of xanthate substitution is only of the order of one xanthate group per two anhydroglucose units. However, higher degrees of substitution and even polyxanthates are possible under special conditions, and the preparation and study of these higher xanthates have permitted a better understanding of the viscose reaction.

If cellulose is treated with certain tetraalkylammonium hydroxide solutions,[28] it disperses completely instead of merely swelling, as when treated with sodium hydroxide solution. When these molecular solutions of cellulose react with CS_2, compounds are formed which have been shown to be the salts of cellulose trixanthic acid corresponding to the particular organic base employed. The reaction depends upon complete dispersion of the cellulose which in turn depends upon the concentration and molecular weight of the organic base. With 3 to 4 N tetraethylammonium hydroxide at 0°C., for example, the reaction is:

$$(C_6H_7O_2(OH)_3)_n + 3n\,(C_2H_5)_4NOH + 3n\,CS_2 \longrightarrow (C_6H_7O_2[OCS_2N(C_2H_5)_4]_3)_n + 3n\,H_2O \qquad (3)$$

The trixanthate formed gives a trixanthogen $([C_6H_7O_5(CS_2)_3]_2)_n$ upon oxidation with iodine. With tetramethylammonium hydroxide, however,

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[27] H. Ost, *Ann.*, **382,** 340 (1911); R. Wolffenstein and E. Oeser, *Ber.*, **56B,** 785 (1923); *Kunstseide,* **7,** 2, 27, 74 (1925); R. Bernhardt, *Kunstseide,* **8,** 173 (1926); E. Heuser and M. Schuster, *Cellulosechemie,* **7,** 17 (1926); T. Lieser, *Ann.*, **464,** 43 (1928); *Cellulosechemie,* **10,** 156 (1929); E. Geiger, *Helv. Chim. Acta,* **13,** 281 (1930); S. Iwasaki, *J. Soc. Chem. Ind., Japan,* **35,** Suppl. binding, 91, 92 (1932); O. Faust, *Ber.*, **62,** 2567 (1929); J. Compton, *Ind. Eng. Chem.*, **31,** 1250 (1939); H. K. Maeda, *J. Soc. Textile and Cellulose Ind., Japan,* **1,** 672, **2,** 8, 13 (1945); O. Samuelson, *Cellulosa och Papper (1908–1948)*, S.P.C.I., pp. 295–325.

[28] T. Lieser, *Chem.-Ztg.*, **60,** 387 (1936); T. Lieser and E. Leckzyck, *Ann.*, **522,** 56 (1936); T. Lieser, *Kolloid-Z.*, **81,** 234 (1937); Rohm & Haas, Brit. Patent 439,806 (Dec. 9, 1935).

dispersion does not occur and the trixanthate is not obtained. With other bases and under other conditions of concentration, dixanthates are formed which upon oxidation with iodine give the dixanthogen $([C_6H_8O_5(CS_2)_2]_2)_n$.

If cellulose is allowed to react with metallic sodium in liquid ammonia and the resulting trisodium derivative is treated with CS_2 under special conditions, a product corresponding to the trixanthate is formed.[29] Also, if sodium cellulose xanthate, as produced commercially with 30 to 40% CS_2 based on the cellulose in the alkali cellulose, is partially dissolved by the addition of NaOH and/or water or completely dissolved to form a normal viscose solution, and this *dispersed* xanthate is treated with further quantities of CS_2 or with a more highly substituted xanthate, the reaction continues and higher degrees of substitution, that is, polyxanthates, result. By "after-xanthating" procedures of this type and even by the direct xanthation of *regenerated* cellulose (as opposed to *native* cellulose) or of alkali cellulose pressed less than normal, products containing up to nearly two xanthate groups per anhydroglucose unit (γ-values[30] up to 180) have been obtained.[31,32]

Thus, the degree of xanthate substitution is in proportion to the dispersion of the reacting cellulose. When the cellulose is completely dissolved, and presumably all OH groups are made available for reaction, a permutoid reaction and a stoichiometric compound, that is, a trixanthate, results. When dispersion is not complete, only the OH groups that are actually available or accessible undergo reaction.

In commercial xanthation, the reaction occurs between CS_2 and *swollen*, i.e., *fibrous*, native cellulose, not *dispersed* cellulose, and all of the OH groups are clearly not equally available. That chemical reaction does occur with conversion of some OH groups to xanthate groups is established by the high temperature coefficient of the reaction, by spectrochemical analysis, by the fact that the reaction curve follows the equation of a unimolecular reaction, and by other data.[22,33] However, the degree of substitution, as mentioned above, is usually only about $1CS_2:2C_6H_{10}O_5$. This is equivalent to 23.5% CS_2 or 19.8% S based on the cellulose, which is in line with concentrations actually used if it is considered that only about 75% of the total CS_2 used reacts with the cellulose. (In Figure 72B, starting with 34% CS_2, a maximum xanthate sulfur content of about 1.65% on the viscose or 22% on the cellulose is indicated.) Moreover, soluble xanthates have been produced with a molar ratio of $CS_2:C_6H_{10}O_5$ of only 1:2.5 (19% CS_2)[22] and it has been claimed that 16% CS_2 and even less is sufficient.[34] But higher degrees of substitution than the ratio 1:2 are also possible with fibrous alkali cellulose. Although good solubility does not require it, $CS_2:C_6H_{10}O_5$ molar ratios of the order of 1:1 are readily produced by increasing the amount of CS_2 and time of reaction sufficiently.[35] (See Fig. 72A which indicates about 2.9% xanthate sulfur in viscose, or 39% on the cellulose, starting with 80% CS_2.)

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[29] P. C. Scherer and L. P. Gotsch, *Bull. Virginia Polytech. Inst.*, **32**, 11 (1939).

[30] The γ-value is the number of xanthate groups per 100 anhydroglucose units; thus a γ-value of 100 is equivalent to 1 mole CS_2 per $C_6H_{10}O_5$, i.e., 46.95% CS_2 (39.5% S) on the cellulose or 3.0% xanthate S in viscose containing 7.5% cellulose. See H. Fink, R. Stahn, and A. Matthes, *Angew. Chem.*, **47**, 602 (1934); N. V. Nederlandsche Kunstzijdefabriek, German Patent 421,506 (Jan. 18, 1922); *Chem. Zentr.*, **97**, **I**, 1332 (1926); L. Lilienfeld, Brit. Patent 212,865 (June 2, 1923); *Chem. Abstracts*, **18**, 2249 (1924).

[31] T. Lieser, *Ann.*, **528**, 276 (1937); W. Schramek and E. Zehmisch, *Kolloid-Beihefte*, **48**, 93 (1938); K. Jung, *Kolloid-Z.*, **108**, 120 (1944); K. Lauer and coworkers, *Kolloid-Z.*, **110**, 26 (1945); **119**, 151 (1950); K. Hess and coworkers, *Naturwissenschaften*, **38**, 433 (1951).

[32] G. Centola, *Atti congr. intern. chim., 10th Congr., Rome*, **4**, 117, 129, 138, 722, 728 (1938).

This does not necessarily mean that stoichiometric compounds of 1:1 or 1:2 ratios are formed. A considerable amount of evidence has been developed to show that the reaction is topochemical or micellar and that only the cellulose in the amorphous areas and/or on the surface of the crystallites reacts. Against this, the conclusion has been reached by others that the reaction takes place also within the crystalline regions and is permutoid or molecular in nature.

Regardless of the final explanation of the reaction mechanism, the importance of alkali cellulose I in industrial xanthation is generally well recognized and established. Attempts to produce a soluble xanthate from fibrous alkali cellulose by using concentrations of NaOH in steeping much above or below 18% have been unsuccessful.[36] However, it is not the con-

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[33] B. Rassow and W. Aehnelt, *Cellulosechemie,* **10,** 169 (1929); K. Atsuki and T. Takata, *J. Soc. Chem. Ind., Japan,* **43,** Suppl. binding, 399 (1940).

[34] A. J. Burette, French Patent 430,221 (May 22, 1911); L. Lilienfeld, U. S. Patent 1,658,607 (Feb. 7, 1928); *Chem. Abstracts,* **22,** 1237 (1928); see also E. Berl and J. Bitter, *Cellulosechemie,* **7,** 137 (1926); K. Hess, *Die Chemie der Zellulose,* Akadem. Verlagsgesellschaft, Leipzig, 1928, p. 326; N. I. Nikitin and T. I. Rudneva, *Compt. rend. acad. sci. U. R. S. S.,* **28,** 240 (1940).

[35] G. de Wyss, *Ind. Eng. Chem.,* **17,** 1044 (1925); O. Faust, *Kolloid-Z.,* **46,** 329 (1928); *Ber.,* **62,** 2572 (1929); J. G. Weeldenberg, *Chem. Weekblad,* **30,** 47 (1933); P. C. Scherer and D. W. Miller, *Rayon Textile Monthly,* **19,** 478 (1938); H. L. Bredée, *Kolloid-Z.,* **94,** 81 (1941); K. Hess, H. Kiessig, and W. Koblitz, *Naturwissenschaften,* **38,** 433 (1951); *Z. Elektrochem.,* **55,** 697 (1951).

[36] K. Atsuki, *Cellulose Ind.* (Tokyo), **7,** 207 (1931); A. Lottermoser, *Z. angew. Chem.* **42,** 1151 (1929).

centration of the NaOH surrounding the alkali cellulose which determines the solubility of the xanthate but the composition of the alkali cellulose crystallites.[37] With 18% NaOH, alkali cellulose I is formed and this compound must be considered the basis of the industrial xanthate reaction.

Alkali cellulose II apparently also reacts with carbon disulfide to produce a soluble xanthate with a $CS_2:C_6H_{10}O_5$ ratio of 1:2, but only at elevated temperature (60°C.). This reaction is possibly even more nonuniform than that of alkali cellulose I. Likewise, if cellulose is sufficiently milled or is xanthated by emulsion techniques, it may be converted to a soluble xanthate by treatment with *dilute* alkali and CS_2 without the prior formation of alkali cellulose I. Although these reactions[38] cannot be ignored, they involve conditions quite different from those encountered in industrial xanthation.

The contention that the reaction is micellar in nature and follows a heterogeneous course is based in part on the ideas that the ratio of NaOH to $C_6H_{10}O_5$ in alkali cellulose I is 1:2, that the maximum degree of substitution of fibrous alkali cellulose is of the order of $1CS_2:2C_6H_{10}O_5$, and that in view of the dispersibility of unxanthated alkali cellulose by cellulose xanthate it is not necessary for *all* the cellulose to react initially with CS_2 to permit good solution. According to this viewpoint,[31,32,37,39] the reaction of fibrous alkali cellulose with excess CS_2 results only in the formation of alkali cellulose IV which is insoluble or, at most, in a degree of substitution of about 0.8 mole of CS_2 per anhydroglucose unit. (Higher degrees of substitution can admittedly be obtained with excess CS_2 but only by adding alkali or water, by further xanthation and/or by redistribution of CS_2 groups after dissolving, and such reactions do lead to penetration of the lattice and a permutoid compound.) Likewise, in commercial alkali cellulose, in which the molar ratio of NaOH to $C_6H_{10}O_5$ is 2:1 (the usual composition is about 15% NaOH–30% $C_6H_{10}O_5$), there is ample Na in the amorphous areas and on the surface of the crystallites to react with all the CS_2 normally used (about 0.75 mole or 35% CS_2 on the cellulose) and thus to account for a 1:2 xanthate. This is true actually whether the ratio of NaOH to $C_6H_{10}O_5$ in alkali cellulose I is 1:2 or 1:1. It is also true even in the formation of a 1:1 xanthate, when excess CS_2 is used, on the basis that the ratio of NaOH to $C_6H_{10}O_5$ in alkali cellulose I is 1:2.

[37] W. Schramek and F. Küttner, *Kolloid-Beihefte*, **42,** 331 (1935).

[38] K. Hess and H. Hepp, *Melliand Textilber.*, **29,** 305, 343 (1948).

[39] J. Frenkel, *Cellulosechemie*, **9,** 26 (1928); P. C. Scherer, *Rayon Textile Monthly*, **27,** 22, 409 (1946); T. Lieser, *Kolloid-Z.*, **94,** 96 (1941); *Ber.*, **74B,** 708 (1941); W. Schramek, *Kolloid-Z.*, **94,** 92 (1941).

The micellar mode of reaction has also been suggested on the basis that:[31,32,37,39–41]

X-ray investigations show that alkali cellulose I is always present in commercial xanthate; even though the alkali cellulose I diagram disappears on long standing, this does not in itself prove that the reaction is molecular.

When cellulose xanthate is methylated and the methylated product is subjected to acetolysis, nearly 50% of unmethylated cellobiose octaacetate is obtained.

Fractionations of viscose with salt solutions (in the author's experience) and of a diethylchloracetamide derivative show the presence of xanthates of various degrees of substitution, precluding the existence of a definite chemical compound in the ordinary sense.

Mercerization is a micellar reaction and cuprammonium solutions of cellulose are micellar.

Molecular and micellar solutions of cellulose have the same viscosity, and changes in viscosity or D.P. do not necessarily mean changes in crystallite size; it is, therefore, not surprising that the $CS_2:C_6H_{10}O_5$ ratio does not change with D.P.

Carbon disulfide reacts with fibrous alkali cellulose only in dissolved form via the free NaOH, first forming dithiocarbonate and the latter then reacting with the alkali cellulose.

Soluble xanthates can be produced without prior formation of alkali cellulose I (see above).

The initial reaction of CS_2 with fibrous alkali cellulose is heterogeneous. The only plausible explanation for such a reaction is that it is topochemical or micellar in nature. Since the crystalline and amorphous areas in cellulose exist in the proportion of approximately 1:1, the $CS_2:C_6H_{10}O_5$ ratio of 1:2 simply reflects the ratio of these areas.

Many of the above arguments for a micellar reaction must be considered of questionable validity in view of the vast amount of contrary data showing that the reaction is molecular in character.[35] The latter viewpoint follows, for example, from data indicating that the ratio of NaOH to $C_6H_{10}O_5$ in

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[40] K. Hess and C. Trogus, *Cellulosechemie*, **13**, 84 (1932); W. Schramek and coworkers, *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 226 (1938); *Z. physik. Chem.*, **B50**, 298 (1941); *Melliand Textilber.*, **28**, 383 (1947); T. Lieser and coworkers, *Kolloid-Z.*, **81**, 240 (1937); *Ann.*, **528**, 284 (1937); *Ann.*, **548**, 204, 212 (1941); K. Jung, *Kolloid-Z.*, **108**, 120 (1944); T. Bergek, *Norsk Skogind.*, **2**, 289 (1948); P. C. Scherer and R. W. Phillips, *Rayon and Synthetic Textiles*, **30**, No. 5, 45 (1949).

[41] T. Lieser, *Ann.*, **470**, 104 (1929); **483**, 132 (1930); K. Lauer and coworkers, *Kolloid-Z.*, **110**, 26 (1945); **119**, 151 (1950).

alkali cellulose I is 1:1 (and not 1:2) and that commercial alkali cellulose (with the usual molar composition of $2NaOH:1C_6H_{10}O_5$) readily forms a 1:1 xanthate with excess CS_2 and sufficient time. This 1:1 reaction must penetrate the alkali cellulose I crystallites as, it is claimed, there is not enough Na outside of the crystalline areas. Xanthation must, therefore, occur also, at least to some extent, within the crystalline areas when less CS_2 is used since there is nothing fundamental about the usual commercial 1:2 xanthate.

Further evidence of the molecular nature of the reaction and arguments against a micellar reaction may be briefly summarized:[30,32,35,42]

X-ray investigations now show that the alkali cellulose I diagram which may be present at first in cellulose xanthate, is due to incomplete reaction and that it disappears completely on standing, even at a low extent of reaction with CS_2.

Fractionation of a diethylchloracetamide derivative by other workers shows uniform distribution of CS_2 groups and little variation in degree of substitution; in a 1:1 xanthate, some glucose residues would have to be even more highly substituted if the reaction occurs only on the surface.

The $CS_2:C_6H_{10}O_5$ ratio does not change with D.P.; this is difficult to explain on the basis of a micellar surface reaction since the area of the surface is not fixed but changes with D.P.

The ratios of the η_{sp}/C values for a series of xanthates of different D.P.s to the η_{sp}/C values of the celluloses regenerated therefrom and dissolved in cuprammonium solution are constant, which could be so only in a molecular reaction.

Alkali cellulose treated with sodium sulfide does not produce a soluble xanthate on reaction with CS_2 even though it has the same crystal structure as normal alkali cellulose.

The formation of higher xanthates in solution does not prove that a fibrous xanthate cannot enter into a molecular reaction as claimed.

In the reaction of alkali cellulose with carbon dioxide, the cellulose reacts completely and the alkali cellulose I crystallites disappear; they therefore should not be a hindrance to reaction with CS_2 in normal xanthation.

The methylation results mentioned above do not prove the presence of unaltered cellulose in the xanthate. They may be explained on the basis that the CS_2 groups are randomly distributed with some glucose units carry-

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[42] G. Centola, *Ann. chim. applicata*, **31**, 525 (1941); H. Staudinger and coworkers, *Ber.*, **71B**, 1995 (1938); *J. prakt. Chem.*, **156**, 261 (1940); O. Samuelson, *Svensk Kem. Tid.*, **58**, 285 (1946).

ing more than one xanthate group and some none. Likewise, the dissolving of unxanthated cellulose in viscose does not mean that the cellulose dissolves as such or prove that the original viscose contained unaltered cellulose. It is due simply to the well-established redistribution of CS_2 groups that occurs after xanthation.

Even though the reaction is nonhomogeneous, it can still be intramicellar or molecular.

With regard to the position of the reactive OH group or groups, the idea that the primary OH group in the 6- position is most capable of undergoing the xanthation reaction was rejected some time ago in favor of the secondary OH group in the 2- position.[41] More recent observations appear to confirm the reactivity of the 2- position in that it reacts first, but only up to a degree of substitution of about $1CS_2:2C_6H_{10}O_5$. After this, the 3- position reacts. Here again, the evidence is not too conclusive. It seems more likely that xanthation does not occur uniformly on any specific OH group but that all three OH groups react and that the CS_2 is randomly distributed.[43] There is some evidence in this connection that although the secondary hydroxyls can and do react initially, the final equilibrium favors the primary hydroxyls.[44]

Most of the evidence developed to date has thus been contradictory and variously interpreted, and it is still not clear exactly what happens in xanthation. Further clarification of the reaction is desirable, including more conclusive data as to the formula for alkali cellulose I and the relative amounts of amorphous and crystalline areas in alkali cellulose. Until then, probably only the trixanthate will be accepted universally as stoichiometric.

For the present, it would appear that the "primary" xanthate reaction in the viscose process involves chemical reaction, but the ratios of $1CS_2:2C_6H_{10}O_5$ usually found in industrial practice and of $1CS_2:1C_6H_{10}O_5$ found as the upper limit in the xanthation of fibrous alkali cellulose do not signify stoichiometric compounds and do not mean that there is necessarily a regular arrangement of the substituent groups along the cellulose chains. For example, the 1:2 product most certainly does not have precisely every second anhydroglucose unit substituted in, say, the 2- position. The real significance of the 1:2 ratio in commercial practice lies only in the fact that this is enough to insure solubility. (The same substitution is required for xanthate as, for example, for carboxymethyl and carboxyethyl substitution. Even nonacid groups such as hydroxyethyl and ethyl give products soluble in 6% NaOH at the 0.5 substitution level.)

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[43] T. Lieser, *Ann.*, **522**, 58 (1936); *Papier-Fabr.*, **36**, Tech.-wiss. Tl., 272 (1938); *Kolloid-Z.*, **94**, 96 (1941).

[44] A. Matthes, *Faserforsch. u. Textiltech.*, **4**, 127 (1952).

In xanthation, initially at least, even with excess CS_2, the xanthate groups are probably distributed at random according to some form of statistical tendency and depending also upon the morphology of the fiber, with the more accessible anhydroglucose units containing perhaps even more than one group. The reaction also involves swelling and physical dispersion of the cellulose, and the resulting compound is probably a mixture of cellulose molecules of varying chain length, substituted to varying degrees.

As was shown in Section A of this Chapter IX, however, the initial distribution of substituents is not the same as the final distribution. Continuous further reaction and redistribution of CS_2 groups occur after initial xanthation so that, on sufficiently long standing or with excess CS_2, the alkali cellulose I crystallites disappear. If the xanthate is dissolved before the reaction is complete, reaction continues in solution and eventually the product is probably molecular in character with the CS_2 groups distributed more or less equally and with most of the crystallites dispersed. Although uniformity of reaction will be approached after a sufficient period of equilibration, the redistribution cannot go to completion with the formation of a perfectly uniform product because of the gradual loss of xanthate groups which takes place during viscose ripening (see below).

In addition to the main reaction between alkali cellulose and carbon disulfide, side reactions also occur during xanthation. These are of two types: (1) secondary reactions of the xanthate itself and (2) direct reaction between CS_2 and free NaOH. The secondary reactions of the xanthate are brought about by its instability and the reversible nature of the reaction with CS_2. The primary reaction (see equation 1) should thus be written as an equilibrium reaction which is forced to the right by increasing the concentration of CS_2. The following secondary reactions of the xanthate also have been suggested:

$$R_{cell}CS_2Na + 2\ NaOH \longrightarrow Na_2CO_2S + NaSH + \text{Cellulose} \tag{4}$$

$$R_{cell}CS_2Na + NaSH \longrightarrow Na_2CS_3 + \text{Cellulose} \tag{5}$$

The thiocarbonate may further react with NaOH forming carbonate and hydrosulfide:

$$Na_2CO_2S + NaOH \longrightarrow Na_2CO_3 + NaSH \tag{6}$$

The other side reaction, between CS_2 and NaOH, may be expressed in the standard way:

$$3\ CS_2 + 6\ NaOH \longrightarrow 2\ Na_2CS_3 + Na_2CO_3 + 3\ H_2O \tag{7}$$

Regardless of the exact nature of these side reactions,[45] the secondary products, which cannot be avoided industrially, consist of carbonate, trithiocarbonate, and probably hydrosulfide and sulfide. The rate of formation of these products is fairly high at the beginning of xanthation but then gradually slows down. They are more stable than the primary xanthate and are responsible for the orange or carrot color of commercial xanthate and viscose. (Pure cellulose xanthate is practically colorless.) In the formation of the xanthate, an equilibrium is undoubtedly reached between it and the secondary products mentioned, although, because of the complicated nature of the mixture, it is difficult to determine satisfactorily the predominating equilibrium. Under normal industrial conditions, about 75% of the CS_2 used reacts with the cellulose and 25% appears as by-products in the *freshly prepared* viscose. (This excludes a small (5–10%) proportion of the CS_2 added which either does not react or is lost mechanically.) Thus, a *fresh* commercial viscose containing 7% cellulose and 2.0% total sulfur (equivalent to 34% CS_2 based on the cellulose) normally shows the presence of about 1.5% xanthate sulfur.

Besides the conversion of OH groups to xanthate groups, colloidal changes occur during xanthation which are characterized by an extraordinary swelling (during which the form of the fiber is partially destroyed), by increased solubility, and by a drop in viscosity. The latter is due to degradation of the cellulose, that is, a reduction in chain length, the extent of the degradation being dependent upon the time, temperature, and amount of oxygen present.

The solution of cellulose xanthate in water or dilute sodium hydroxide solution may be considered simply as a continuation of the swelling process which started with the formation of alkali cellulose. From a colloidal standpoint it is essentially a peptization of a hydrophilic colloid. However, the xanthation reaction apparently continues, probably intramicellarly in part, during and after solution, between unchanged alkali cellulose and CS_2 and/or by redistribution of xanthate groups.[31,32,46] Dispersion of the xanthate is, therefore, a gradual process and continues for some time after the dissolving step. On this basis it may be said that only when solution is complete does true or final xanthate formation occur. It has also been suggested that association takes place during solution and that NaOH or H_2O is combined chemically with conversion of the C═S group to HO—C—SNa or HO—C—SH. X-ray data, however, do not indicate that any new chemical compound is produced.[37,47]

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[45] M. Ragg, *Chem.-Ztg.*, **32**, 630, 654, 677, 730 (1908); **34**, 82 (1910); H. Leuchs, *Kunstseide*, **7**, 286 (1925); G. Kita and R. Tomihisa, *Cellulose Ind.* (Tokyo), **2**, 26 (1926); *Cellulosechemie*, **10**, 134 (1929).

[46] I. Sakurada and R. Inoue, *J. Soc. Chem. Ind., Japan*, **35**, Suppl. binding, 127 (1932); O. Kratky and coworkers, *Kolloid-Z.*, **98**, 301 (1941); W. Schramek and E. Zehmisch, *Kolloid-Beihefte*, **48**, 93 (1938).

The actual degree of dispersion of the xanthate after dissolving in dilute sodium hydroxide solution, i.e., the nature and structure of the xanthate solution, has been the subject of the same controversy as the primary xanthate reaction itself (see above) and is still open to question. On the basis that the reaction between alkali cellulose and CS_2 is micellar, the xanthate solution may also be considered to be made up of micellar or polymolecular particles. This viewpoint is in line also with the analogous viscosity behavior of viscose and micellar soap solutions, the idea that only a low degree of xanthate substitution is possible or necessary for solution in fibrous xanthates, the formation of water-soluble cellulose by dialyzing the product obtained by xanthating cellulose swollen in quaternary ammonium bases and the fact that only alkali cellulose I or cellulose hydrate (depending upon the conditions of coagulation) have been found in the solution by x-ray examination (even though the x-ray diagram of alkali cellulose I disappears on standing). It means that solution overcomes the fiber bond but does not necessarily destroy the alkali cellulose I crystallites.[32,39–41,48]

As in the case of the initial xanthate reaction, considerable evidence is available, on the other hand, indicating that the above ideas are not valid and that the solution is of a molecular nature, i.e., polymer analogous reactions, redistribution of CS_2 groups, the fact that with excess CS_2 the xanthate reaction occurs intramicellarly, that on sufficiently long standing the alkali cellulose I lines in viscose disappear from the x-ray diagram, that dispersion cannot occur without previously overcoming the cohesive forces between the cellulose chains, etc.[32,35,42,49]

[47] B. Rassow and W. Aehnelt, *Cellulosechemie,* **10,** 169 (1929). See also P. Herrent and G. Jnoff, *J. Polymer Sci.,* **3,** 834 (1948).

[48] W. Schramek and coworkers, *Papier-Fabr.,* **36,** Tech.-wiss. Tl., 226 (1938); *Kolloid-Z.,* **94,** 92 (1941); *Z. physik. Chem.,* **B50,** 298 (1941); *Melliand Textilber.,* **28,** 383 (1947); T. Lieser and coworkers, *Cellulosechemie,* **18,** 121 (1940); *Z. physik. Chem.,* **B74,** 708 (1941); *Ann.,* **548,** 195, 212 (1941); *Chem.-Ztg.,* **67,** 197 (1943); *Kolloid-Z.,* **94,** 96 (1941); **98,** 142 (1942); **108,** 125 (1944); P. C. Scherer, *Rayon Textile Monthly,* **27,** 74, 409 (1946); K. Lauer and coworkers, *Kolloid-Z.,* **112,** 112 (1949); R. Vuori, Dissertation, Helsinki (1947).

[49] S. M. Lipatov and N. A. Krotova, *Melliand Textilber.,* **15,** 553 (1934); H. Staudinger and F. Zapf, *J. prakt. Chem.,* **156,** 261 (1940); G. Centola, *Boll. sci. facoltà chim. ind., Bologna,* **1941,** 7–12; O. Samuelson, *Svensk Papperstidn.,* **48,** 517 (1945); F. Gärtner and O. Samuelson, *Svensk Papperstidn.,* **53,** 635 (1950).

Other suggestions concerning the nature of the solution include the ideas that the particles present are *aggregates* of molecular chains, lattice-like particles and characteristic of so-called ''fringe micellae'' and that they are ''cellulose-chain mixed bodies.''[50]

Summarizing the various viewpoints, it appears that dispersion of the xanthate and the structure of the solution vary according to circumstances. Commercial viscose, in which the cellulose concentration is high, is probably a mixture of some micellar (polymolecular) particles and molecular aggregates, the solution being the result of an equilibrium following redistribution of CS_2 groups after xanthation and the dissolving of the unxanthated portions of the alkali cellulose, and aggregation of any individual molecules that may be formed. The cellulose is, or at least need be, only partly xanthated in such solutions since solubility is achieved by dispersion of the unxanthated portions of the cellulose chains by the highly hydrophilic xanthate groups. It does not seem likely under these conditions that dispersion to a wholly molecular condition occurs. Although many individual molecules may be present in a fresh solution, association probably occurs almost at once. In xanthate solutions in which the cellulose concentrations are sufficiently low and/or in which the cellulose is more highly substituted ($CS_2:C_6H_{10}O_5$ ratios of 1:1 or more and certainly for the trixanthate) the dispersion would be expected to be much more complete than in commercial viscoses and under these conditions the solutions are more likely to be, and probably are, almost entirely molecular in nature. In any case, the dispersion or solubility is influenced by practically every variable in the process, including type of cellulose, steeping, pressing, shredding, degree of xanthate substitution, mixing conditions, and viscose composition.

In addition to its effect on the dispersion of the cellulose, the composition of the viscose in cellulose and free NaOH also affects the rate of ripening, the viscosity, the regenerating characteristics (spinning, casting, etc.), and the properties of the regenerated product. Other factors being constant, rate of ripening, viscosity, and reciprocal filterability increase with increase in cellulose concentration or with decrease in free NaOH concentration. Spinning and film-casting properties depend on the ratio of cellulose to caustic as well as upon the absolute concentrations, and a proper balance must be maintained between these constituents and the composition of the coagulating medium used. In comparison, for example, with cellulose acetate, the optimum concentration of cellulose in viscose is relatively low, being in the range of 6 to 10%. Attempts to employ more highly concentrated solutions have been unsuccessful.

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[50] H. L. Bredée, *Kolloid-Z.*, **94,** 81 (1941); J. J. Stöckly, *Kolloid-Z.*, **105,** 190 (1943); M. Takei, *Kolloid-Z.*, **106,** 30 (1944); W. P. Conner and P. I. Donnelly, *Ind. Eng. Chem.*, **43,** 1136 (1951).

3. Characteristics and Reactions of Viscose

Viscose is a sirupy, oily, orange- or carrot-colored solution, with a characteristic odor which is due, in part, to hydrogen sulfide and polysulfides. It possesses many of the characteristics of a typical polyelectrolyte, such as high and anomalous viscosity, relative stability toward electrolytes, syneresis, weak electric charge, flow birefringence, and relatively great conductivity, and it undergoes various chemical and colloidal reactions.

(a) VISCOSE VISCOSITY

The viscosity of viscose depends upon several factors, the more important of which are the D.P. of the cellulose (determined by the type of cellulose, alkali cellulose aging conditions, etc.), the cellulose content, the degree of dispersion (alkali content and other factors influencing dispersion), temperature, and degree of ripening. The actual viscosity used in practice varies with different producers and with the nature of the product to be made. In addition to the requirements of the mechanics involved in transferring the solution through pipe lines and in filtration, evacuation, spinning, casting, and similar operations, there is an optimum viscosity for every combination of production factors (e.g., viscose composition, coagulating bath, and speed of extrusion). From the standpoint of the strength and durability of the regenerated product, the use of a relatively high viscosity (high and uniform cellulose chain length) would seem desirable, but to date both mechanical and chemical difficulties have made it impossible to achieve optimum conditions in this respect. As a result, commercial viscoses range from 30 to 60 poises in viscosity, the weight-average D.P. of the regenerated cellulose varying from about 250 to 600.[51]

The dependence of viscosity on the D.P. of the cellulose is well known and need not be discussed here. The relationship of the viscosity to the concentration of *dilute* viscose solutions is probably analogous to that of other cellulosic solutions (see Chapter X, Sections E and F). Whether any of the equations so far proposed relating viscosity, concentration, and D.P. give more than approximate results with industrial viscose solutions containing 6–10% cellulose remains to be more clearly established. In this connection it should be mentioned that the intrinsic viscosity $[\eta]$ or

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[51] H. Schwartz and H. A. Wannow, *Kolloid-Z.*, **97**, 193 (1941); **99**, 190 (1942).

K_m constant of viscose apparently varies depending upon the degree of xanthate substitution, being higher with lower substitution.[52]

Viscosity is also dependent upon degree of dispersion, and hence the alkali content, of the viscose.[53] Although radical reduction in the viscosity of a viscose, after preparation, is not possible except by degrading the cellulose (indicating that the cellulose in viscose is partially in the form of a molecular dispersion), slight but important changes in viscosity can be produced by altering the NaOH concentration. Increasing the NaOH content from 4 to 6%, for example, decreases the viscosity about 35%, The degree of dispersion, and hence stability, of viscose is greatest at a concentration of about 9% free alkali and at this concentration the viscosity is at a minimum (i.e., the viscosity increases both above and below about 9% NaOH). (For a further discussion of the effect of NaOH concentration on the viscosity of viscose as well as of the behavior of cellulose xanthate as a polyelectrolyte, see Chapter X-C. Since cellulose itself shows its maximum solubility in caustic at a NaOH concentration of about 9% the minimum viscosity at this point undoubtedly reflects the solubilizing influence of the NaOH on unsubstituted portions of the chains and on portions of the sample that were incompletely xanthated.)

Although the characteristic viscosity change during viscose ripening (see below) does not involve the D.P. of the cellulose, viscose viscosity may be affected by the presence of air.[44,54] This is due perhaps to oxidation of the by-products but there is also some evidence that it is possible actually to reduce the D.P. of the cellulose somewhat by atmospheric oxygen, if contact is intimate enough, with some reduction in viscosity.

Like other cellulose and high-polymer solutions, and as might be expected of a polyelectrolyte, viscose exhibits pronounced structural viscosity.[55] That is, in addition to the factors already discussed, its viscosity is related to its gel structure and is a function of rate of flow, decreasing markedly as the velocity gradient or rate of shear increases. This effect is negligible in the *measurement* of viscosity as carried out industrially since the shearing stresses involved here are relatively low and under these conditions the solution is Newtonian. However, structural viscosity is a factor in the passage of viscose through pipe lines and pumps and particularly in the spinning of rayon where the solution passes through spinneret holes at pressures usually exceeding 25 lb./sq. in. Under the latter conditions the viscosity may be only $^1/_{10}$ to about $^1/_{25}$ of that determined by, say, a ball-fall test. Due to deviations from laminar flow, the viscosity reduction in spinning is probably not actually as great as might be expected from the pressures involved. In any case, if it were not for this great reduction in viscosity, the spinning pressures required would be many times higher than those normally used. Also, because of the anomalous flow characteristics of viscose, different viscosities caused by alkali cellulose aging tend to be equalized in spinning.

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[52] H. Staudinger and coworkers, *Ber.*, **71B**, 1995 (1938); *J. prakt. Chem.*, **156**, 261 (1940); W. Philippoff and H. E. Krüger, *Kolloid-Z.*, **88**, 215 (1939); G. Jayme and J. Wellm, *Kolloid-Z.*, **107**, 163 (1944); M. Takei, *Kolloid-Z.*, **106**, 30 (1944).

[53] H. Staudinger and F. Zapf, *J. prakt. Chem.*, **156**, 261 (1940); E. Heuser and H. Y. Charbonnier, *Ind. Eng. Chem.*, **33**, 402 (1941); T. Bergek, *Norsk Skogind.*, **2**, 289 (1948); C. W. Tait and coworkers, *J. Polymer Sci.*, **7**, 261 (1951).

[54] A. Lottermoser and F. Schwarz, *Z. angew. Chem.*, **43**, 18 (1930); *Kolloid-Beihefte*, **42**, 419 (1935); O. Samuelson, *Svensk Papperstidn.*, **47**, 597 (1944).

[55] W. Philippoff and coworkers, *Cellulosechemie*, **17**, 57 (1936); *Kolloid-Z.*, **88**, 215 (1939); H. Staudinger and F. Zapf, *J. prakt. Chem.*, **156**, 261 (1940); H. L. Bredée and J. de Booys, *Kolloid-Z.*, **96**, 24 (1941); H. Erbring, *Kolloid-Z.*, **108**, 152 (1944); A. Lude, *Rec. trav. chim.*, **68**, 1030 (1949).

In this connection, the flow curve of viscose (shearing force versus velocity gradient) is said to show two points of inflection, suggesting the presence in viscose of two types of particles, *primary* molecules or micelles and *secondary* aggregates. This, however, does not appear to be in line with the observation that only one optical relaxation time has been observed in a well-dissolved solution. It should also be noted that the drop in viscosity which occurs at high shearing stresses (high flows, agitation, or other mechanical action) and which is due to an alteration of the gel structure is reversible. The original viscosity is restored on further standing, and this process can be repeated (suggesting further that viscose may also be thixotropic).[56,57]

(b) VISCOSE RIPENING

One of the most important characteristics of viscose is its instability. From the previous discussion it will be clear that cellulose xanthate is unstable, beginning to decompose immediately after formation, and that viscose is a complicated mixture of cellulose xanthate, NaOH, CS_2, and compounds formed by the interaction of these materials (discussed above). During the ripening of viscose, spontaneous decomposition of the xanthate continues and all of these materials undergo further reaction. These changes are both chemical and colloidal in nature.

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[56] T. Bergek and T. Ouchterlony, *Svensk Papperstidn.*, **49**, 470 (1946); but see also P. Herrent and coworkers, *Research* (London), **2**, 486 (1949) and A. Lude, *Rec. trav. chim.*, **68**, 1030 (1949).

[57] R. Signer and W. Meyer, *Helv. Chim. Acta*, **28**, 328 (1945); V. E. Gonsalves, *Proc. Intern. Congr. Rheology, 1948*, **2**, 239 (1949); W. P. Conner and P. I. Donnelly, *Ind. Eng. Chem.*, **43**, 1136 (1951).

(*1*) *Chemical Changes*

The most important chemical change is the decomposition of the cellulose xanthate itself which results in the gradual splitting off of CS_2 and regeneration of the cellulose. As might be expected in the case of a substance made up of a strong base and a weak acid, the reaction is predominantly a hydrolysis reaction,[27,44,47,58] with the formation of free cellulose xanthic acid and NaOH until an equilibrium is reached according to:

$$\frac{[\text{Sodium cellulose xanthate}][H_2O]}{[\text{Xanthic acid}][NaOH]} = K \qquad (8)$$

Since the free xanthic acid is also unstable, liberating CS_2, the reaction is forced to the right, and more and more xanthate is decomposed, until finally the regeneration of the cellulose is complete. The reactions may be represented by the following equations:

$$R_{cell}OCSSNa + H_2O \longrightarrow R_{cell}OCSSH + NaOH \qquad (9)$$

$$R_{cell}OCSSH + H_2O \longrightarrow HOCSSH + \text{Cellulose} \qquad (10)$$

$$HOCSSH \longrightarrow CS_2 + H_2O \qquad (11)$$

The same end products result by saponification, which also occurs to a slight extent, being more noticeable as the caustic content of the viscose increases:

$$R_{cell}OCSSNa + H_2O \longrightarrow HOCSSNa + \text{Cellulose} \qquad (12)$$

$$HOCSSNa \longrightarrow CS_2 + NaOH \qquad (13)$$

This decomposition of the xanthate during ripening, as represented by the changes in xanthate sulfur content, is shown graphically in Figure 74A. In practice, the hydrolysis is not allowed to proceed to completion. Thus, a 7% cellulose viscose for use in rayon, containing initially approximately 1.5% xanthate sulfur (2.0% total sulfur), is normally ripened until the xanthate sulfur content reaches 0.9 to 1.1%. This represents a change in the average degree of esterification from about $1CS_2:2C_6H_{10}O_5$ to $1CS_2:3C_6H_{10}O_5$. For many purposes, the viscose is used even before the xanthate sulfur has reached this range.

The redistribution of CS_2 groups which occurs during ripening has already been mentioned and need not be further discussed. Besides this and the decomposition of the xanthate, other chemical changes occur dur-

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[58] B. Rassow and M. Wadewitz, *J. prakt. Chem.*, **106**, 266 (1923); R. Bernhardt, *Kunstseide*, **7**, 193 (1925); **8**, 257, 314 (1926); J. Frenkel, *Cellulosechemie*, **9**, 25 (1928); W. Klauditz, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 251 (1939); W. Vieweg, *Papier-Fabr.*, **37**, Tech.-wiss. Tl., 269 (1939).

ing ripening, involving the secondary products. The formation of sodium trithiocarbonate and carbonate continues by reaction between NaOH and the CS_2 liberated from the free xanthic acid. Other by-products may include sodium sulfide, polysulfide, and thiosulfate. Whether sulfide originates as an intermediate in the formation of Na_2CS_3 or as the result of the decomposition of the trithiocarbonate is not certain but its presence in viscose is reasonably well established. These side reactions have been variously represented, in addition to equation 7 as follows:[27,45,47,59]

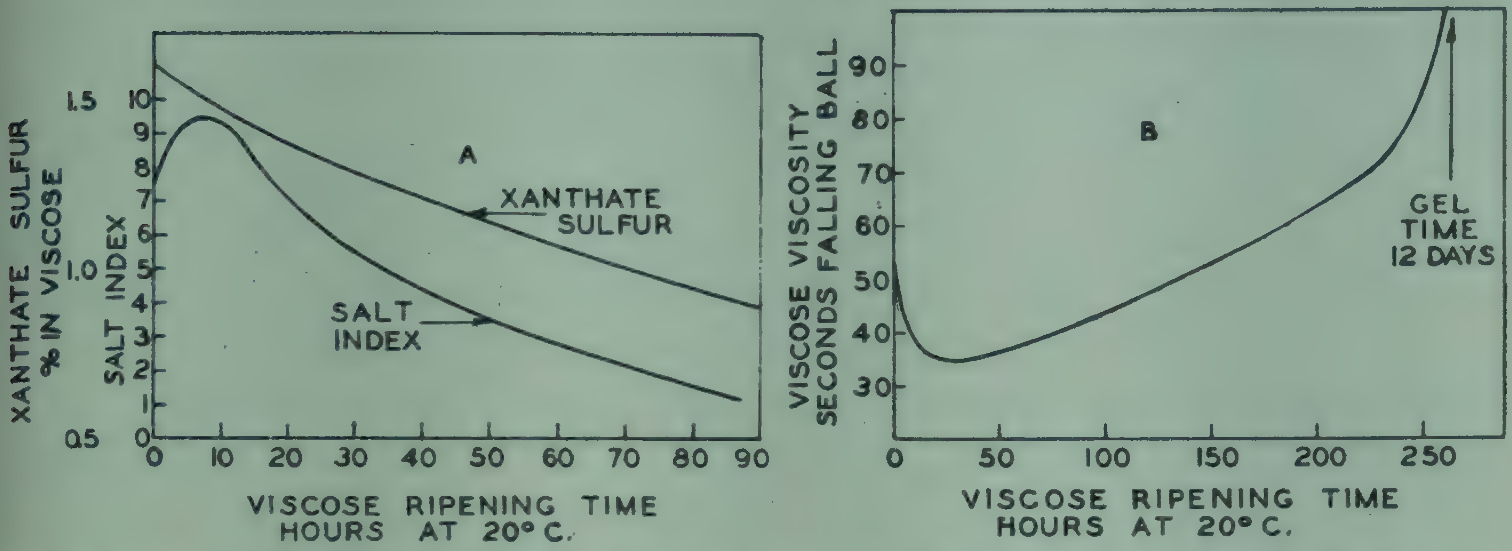

Fig. 74. Changes during viscose ripening:[15] (A) in salt index and xanthate sulfur content; (B) in viscosity. Courtesy of Research Division, Rayonier Incorporated

$$5\ CS_2 + 12\ NaOH \longrightarrow Na_2S + 2\ Na_2CO_3 + 3\ Na_2CS_3 + 6\ H_2O \quad (14)$$

$$CS_2 + Na_2S \longrightarrow Na_2CS_3 \quad (15)$$

$$\left.\begin{array}{rcl} Na_2CS_3 + 3\ H_2O & \longrightarrow & Na_2CO_3 + 3\ H_2S \\ & \text{or} & \\ Na_2CS_3 + 2\ H_2O & \longrightarrow & H_2CS_3 + 2\ NaOH \\ H_2CS_3 & \longrightarrow & H_2S + CS_2 \end{array}\right\} \quad (16)$$

$$Na_2CS_3 + 3\ NaOH \longrightarrow 3\ NaHS + Na_2CO_3 \quad (17)$$

$$CS_2 + 2\ NaHS \longrightarrow Na_2CS_3 + H_2S \quad (18)$$

$$CS_2 + H_2O \longrightarrow H_2S + COS \quad (19)$$

The chemical changes may then be summarized by saying: In xanthation, sodium cellulose xanthate and by-product salts are formed side by side,

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[59] B. Rassow and K. Schwarze, *Papier-Fabr.*, **28,** Tech.-wiss. Tl., 746 (1930); H. Lotze, *Kunstseide,* **15,** 194 (1933); C. L. Moore, *Silk and Rayon,* **8,** 505, 563 (1934); O. Samuelson, *Cellulosa och Papper 1908–1948* S.P.C.I., pp. 295–325; R. S. Neumann and coworkers, *Cellulosechemie,* **17,** 16 (1936). For spectrochemical changes during ripening see K. Atsuki and T. Takata, *J. Soc. Chem. Ind., Japan,* **43,** 402B (1940); B. Rassow and W. Aehnelt, *Cellulosechemie,* **10,** 169 (1929); P. Herrent and G. Jnoff, *J. Polymer Sci.*, **3,** 487 (1948).

with free CS_2 and NaOH remaining. After solution, new NaOH is added. Even though xanthate formation takes place more rapidly than the other reactions the xanthate, being very unstable, is also decomposed faster than the secondary products. Xanthate sulfur content and free NaOH, therefore, decrease markedly, while the salt content increases. Several equilibriums are established until all the CS_2 has been converted and then a "salting out" effect sets in, due to the various salts present, which results eventually in precipitation of the cellulose as cellulose hydrate.[60]

(2) *Colloidal Changes*

As a hydrophilic colloid, viscose also undergoes significant changes in its colloidal properties during ripening. It has even been suggested that the colloidal processes predominate at first and induce the chemical changes,[61] although this seems doubtful.

One of the most peculiar colloidal changes during viscose ripening is that involving the viscosity of the solution, which at first drops rather rapidly, then passes through a minimum point, and finally rises slowly until coagulation is complete. This course of the viscosity change during the ripening of a representative commercial viscose is shown in Figure 74B, but it should be understood that the shape of the curve may differ somewhat from that shown depending upon viscose composition, temperature, CS_2 concentration, dissolving time, and other factors. The change in viscosity is not due to any change in the degree of polymerization of the cellulose. Although some degradation of the cellulose occurs in every other step of the process, little, if any, occurs during ripening.[62] The initial drop in viscosity has been explained on the basis that solution of the xanthate is a slow process and requires time or that final xanthate formation does not take place until solution occurs. Even though the xanthate apparently dissolves during the mixing operation, the dispersion is "coarse" and incomplete. Further solution, including penetration of the alkali cellulose crystallites, continues for 24 to 48 hrs., due either to continued progress of the CS_2 reaction or redistribution of the CS_2 groups, or both[32,39] (which may explain the hump in the first part of the salt index curve in Figure 74A), until the disintegration is complete, the viscosity decreasing as the dispersion approaches an optimum. In some cases the viscosity may actually rise slightly for a short time before the drop just described. This rise has been attributed to a further increase in the degree of hydration of the cellulose, and the initial decrease in viscosity may conceivably be simply the result of dehydration of the dispersed particles, that is, a decrease in the amount of water held by the internal dispersed phase due to osmosis.[61,63]

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[60] There is some evidence indicating that conversion of alkali cellulose I to cellulose hydrate occurs during ripening by way of alkali cellulose IV; see W. Schramek, *Kolloid-Beihefte*, **42**, 331 (1935). It should be added also that viscose may absorb atmospheric oxygen during ripening with the formation of the disulfide, $R_{cell}OCSS—SSCOR_{cell}$, and some thiosulfate; see S. N. Danilov and coworkers, *J. Gen. Chem.* (*U. S. S. R.*), **19**, 826 (1949); also, References 44 and 54.

[61] K. Atsuki, *J. Faculty Eng., Tokyo Imp. Univ.*, **17**, 135 (1927); *Cellulosechemie*, **9**, 106 (1928).

[62] E. Heuser and M. Schuster, *Cellulosechemie*, **7**, 17 (1926); S. Rogowin and M Schlachover, *Cellulosechemie*, **14**, 17, 40 (1933); A. Lottermoser and F. Wultsch, *Kolloid-Z.*, **83**, 180 (1938); H. Staudinger and coworkers, *Papier-Fabr.*, **36**, 557 (1938); *Ber.*, **71B**, 1995 (1938); *J. prakt. Chem.*, **156**, 261 (1940); J. Compton, *Ind. Eng. Chem.*, **31**, 1250 (1939).

The subsequent increase in viscosity is due to the opposite effect, that is, a decrease in solubility. As hydrolysis proceeds, causing the ratio of combined sulfur to cellulose to become constantly smaller, the fraction of the chain that becomes unsubstituted and hence insoluble becomes constantly greater, and the degree of dispersion of the cellulose decreases due to association and aggregation, until visible coagulation sets in. The increase in viscosity which takes place is thus the manifestation of the decreasing solubility and increasing degree of cross-linking of the cellulose molecules, and is not the result of change of molecular weight. Additional evidence of the nature of these changes is shown by the formation of gel structure, changes in flow birefringence, and other characteristics during ripening,[57,64] and by the fact that the original viscosity may be restored (in fact, the whole ripening process may be reversed) by adding CS_2 to viscose at any stage of the process. This does not mean that no chemical reactions are involved since it is clear that the changes in degree of substitution which occur are responsible, at least in part, for the viscosity changes.

Perhaps the most significant colloidal change in viscose during ripening is the change in its coagulation properties. As initially prepared, viscose is relatively stable and difficult to coagulate. Paralleling the chemical changes mentioned above, however, the solution coagulates spontaneously by virtue of the constantly decreasing solubility of the dispersed phase and increasing salt formation. Since the —CSSNa group is the solubilizing factor in the xanthate molecule (the cellulose itself is insoluble), as the

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[63] C. J. J. Fox, *J. Soc. Chem. Ind.*, **49**, 83T (1930); see also J. J. Stöckly, *Kolloid-Z.* **105**, 190 (1943); T. Bergek and T. Ouchterlony, *Svensk Papperstidn.*, **49**, 470 (1946).

[64] E. Berl and A. Lange, *Cellulosechemie*, **7**, 145 (1926); J. J. Stöckly, *Kolloid-Z.*, **105**, 190 (1943); G. Centola, *Boll. sci. facoltà chim. ind., Bologna*, **1941**, 7–12; M. Takei, *Kolloid-Z.*, **106**, 30 (1944).

number of —CSSNa groups per anhydroglucose unit decreases, the solubility of the material decreases. If ripening is allowed to proceed uninterruptedly and all the —CSSNa groups are split off, it becomes completely insoluble, and the solution is converted completely and spontaneously to a gel of hydrated cellulose. The rate of this change and the actual time required for gelation will vary considerably, depending upon such factors as temperature, type and D.P. of the original cellulose, viscose composition, oxygen and CS_2 content; i.e., the higher the D.P., the oxygen and cellulose contents, and temperature are, the faster is the ripening; the higher the NaOH and CS_2 contents are, the slower is the ripening.

As spontaneous coagulation proceeds during ripening, the hydrophilic character of the solution decreases and it becomes more and more hydrophobic in nature. This change is manifested by increasing instability and ease of coagulation with various agents such as acetic acid, alcohols, and inorganic salts. Being the salt of a stronger acid, the xanthate is not (readily) decomposed by monocarboxylic acids of the fatty series such as formic, acetic, and lactic acids, or by CO_2, SO_2, and other weak acids. (These acids do react with the free NaOH and decompose the by-product sodium salts with the formation of the sodium salts of the acid used and liberation of CS_2, H_2S, and CO_2.) Moreover, these acids do not usually coagulate freshly prepared viscose. As ripening proceeds, however, a point is reached where addition of an acid such as acetic also causes coagulation, and, as ripening continues, lesser and lesser amounts of acid are required for coagulation.

Methyl and ethyl alcohols, and alkali and ammonium salts, also coagulate viscose, precipitating the xanthate unchanged. This behavior is entirely analogous to that of other polyelectrolytes such as carboxymethyl cellulose and proteins. With inorganic salts, coagulation is based on a "salting-out" effect (dehydration of the dispersed phase) which follows an initial neutralization of the negatively charged xanthate particles by the first addition of the electrolyte. Whereas large amounts of alcohol and salts are required to coagulate the viscose when freshly prepared, lesser and lesser amounts are necessary as ripening progresses and the hydrophobic character of the solution increases. This change is shown by the salt index curve in Figure 74A. As initially prepared, about an 8.0% NaCl solution is required for coagulation of a drop of this particular viscose. After 45 hrs., a 4.0% salt solution suffices, and after about 75 hrs. only a 2.0% solution is required. When 10% NH_4Cl is added to the same viscose solution, 27.2 cc., 10 cc., and 6.4 cc. are needed for coagulation after the respective ripening times. Tests based on these coagulation properties are described below.

Among other characteristics of viscose, to which reference has been made, is flow birefringence. Even at low rates of shear, viscose shows marked optical double refraction, and studies of the magnitude of the birefringence, of relaxation times, and related properties, permit certain conclusions regarding the structure of the solution and the changes in the structure during viscose ripening and spinning.[57] As might be expected, flow birefringence and optical relaxation time increase during ripening. It may be added that it has been found in certain viscoses that the curves for relative viscosity and the precipitation potential of silver xanthate as functions of ripening time both pass through a minimum at the same degree of ripening. This suggests that there may be an "optimum structure" for obtaining optimum mechanical properties of the end products at this particular degree of ripening but just what this structure is has not yet been established.[65]

Other changes during ripening include syneresis, increased turbidity, increased particle size, decreased dissociation, decreased conductivity, and changes in light absorption, Tyndall effect, Brownian movement, and volume.[66]

(3) *Control of Ripening*

Since the spinning and casting properties of viscose as well as the quality and characteristics (tenacity, elongation, luster of filaments, clarity of films, dyeing, softness, etc.) of the end product (rayon, cellophane) are determined in part by the degree of ripening, the normal instability of viscose is a major source of concern in its industrial utilization. For this reason, precautions are taken to maintain constant conditions (constant salt index) and to inhibit or retard ripening. This is usually accomplished mechanically by such measures as the use of relatively low viscose temperatures (15–20°C.) during ripening, refrigeration and stepwise reduction in size of supply lines, and blending of batches (including the recirculation of viscose around the spinning machines and feed tanks). Chemical methods may also be used to retard ripening. It has been mentioned that the CS_2 and free alkali concentration influence ripening; the higher the content of NaOH (up to about 9%) and the higher the CS_2 are, the more stable is the viscose and the slower is the ripening. Other materials which have been proposed for addition to viscose to retard ripening include sodium sulfite, sodium cyanide, arsenites, certain urea and other amino derivatives, alkyl xanthates, phenols, calcium acetate, gallic acid, acrylonitrile, pyridine, and others.[67,68] With the exception of sodium sulfite, however, none of these addition agents appears to be used in practice.

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[65] P. Herrent and coworkers, *Research* (London), **2,** 486 (1949). See also W. Schramek, *Melliand Textilber.*, **28,** 420 (1947) for other changes in structure during ripening.

[66] T. Mukoyama, *Kolloid-Z.*, **41,** 62 (1927); **42,** 79, 180, 353 (1927); S. M. Lipatov, *Kolloid-Z.*, **49,** 441 (1929); R. Bernhardt, *Melliand Textilber.*, **7,** 55, 318 (1926); T. Sugita, *Cellulose Ind.* (Tokyo), **8,** 3, 166 (1932); R. O. Herzog, *Kolloid-Z.*, **35,** 193 (1924); Schwedler, Dissertation, Leipzig, 1927; B. Rassow and W. Aehnelt, *Cellulosechemie,* **10,** 169 (1929); K. Atsuki and T. Takata, *J. Soc. Chem. Ind., Japan,* **43,** 402B (1940); G. Centola, *Boll. sci. facoltà chim. ind., Bologna,* **1941,** 7–12; P. C. Scherer, *Rayon Textile Monthly,* **26,** 69, 117 (1945).

Consideration has been given also to methods for accelerating ripening in order to reach the desired degree of esterification more rapidly and thus to reduce or even eliminate the ripening step. It is obvious that this can be done in several ways, such as by raising the ripening temperature, by adding electrolytes, and by using low concentrations of NaOH and CS_2.[69] The addition to viscose of hemicellulose, polyalcohols like glycerol, ether, hydrogen peroxide, sulfide, polysulfides, air, and other materials[44,70] also accelerates ripening. Although the effect of some of these agents may be colloidal in nature, the action of most of the above-mentioned ripening accelerators and inhibitors is due to an actual change in rate of chemical decomposition of the xanthate.[68]

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[67] C. A. Ernst, U. S. Patent 863,793 (Aug. 20, 1907); *Chem. Abstracts*, **2,** 478 (1908); R. W. Maxwell, U. S. Patent 2,011,227 (Aug. 13, 1935); *Chem. Abstracts*, **29,** 6758 (1935); R. Linkmeyer and H. Hoyermann, German Patent 312,392 (Nov. 17, 1917); *Chem. Zentr.*, **90, IV,** 1017 (1919); Soc. Lorch and Hamm, French Patent 728,682 (Dec. 21, 1931); *Chem. Abstracts*, **26,** 6137 (1932); E. B. Castillo, *Anales fis. y quím.* (*Madrid*), **43,** 60 (1947).

[68] For the action of acrylonitrile see J. P. Hollihan and S. A. Moss, Jr., *Ind. Eng. Chem.*, **39,** 222 (1947); J. H. MacGregor and C. Pugh, *J. Soc. Dyers Colourists*, **64,** 71 (1948).

[69] C. A. Ernst, U. S. Patents 896,715 (Aug. 25, 1908); 863,793 (Aug. 20, 1907); *Chem. Abstracts*, **2,** 478 (1908); Vereinigte Kunstseide-Fabriken Akt.-Ges., Brit. Patent 17,502 (Aug. 8, 1902); Société Française de la Viscose, Brit. Patent 8179 (1907); *Chem. Abstracts*, **2,** 1762 (1908); Soc. Anon. Soie de St. Chamond, Brit. Patents 1436 (Aug. 10, 1910); 24,291 (Dec. 18, 1914); *Chem. Abstracts*, **10,** 1600 (1916); Deutsche Zellstoff-Textilwerke, German Patents 339,050 (Oct. 12, 1918); *Chem. Zentr.*, **92, IV,** 669 (1921); 342,641 (Oct. 30, 1919); *Chem. Zentr.*, **93, II,** 48 (1922); W. Mendel, German Patent 566,691 (Aug. 30, 1930); *Chem. Abstracts*, **27,** 2578 (1933); A. J. Burette, French Patent 430,221 (May 22, 1911); J. A. Calhoun, Jr., and F. C. Wedler, U. S. Patent 2,558,037 (June 26, 1951); *Chem. Abstracts*, **45,** 7791 (1951).

[70] R. L. Cairncross and G. H. Goodell, U. S. Patent 1,814,543 (July 14, 1931); T. Mukoyama, *Kolloid-Z.*, **42,** 180 (1927); J. Sauvy, *Ind. textile*, **63,** 143 (1946); O. Samuelson, *Cellulosa och Papper 1908–1948*, S.P.C.I., pp. 295–325.

(c) PURIFICATION OF VISCOSE

Various suggestions have been made for the purification of viscose and the preparation of cellulose xanthate in a stable, dry form free from the usual by-product salts. Viscose can be coagulated with alcohol, salts, or a weak acid, or a combination of these agents, and the by-products can be removed by washing the precipitated xanthate with fresh precipitating solution. The washed xanthate may then be redissolved in caustic solution or dried if desired. Such procedures are of interest in studying the composition of the xanthate and viscose, since purified, dried xanthate is reasonably stable. Although a number of purification methods have been described and patented,[27,30,71] they are expensive, and they are superfluous so far as the major technical applications of viscose are concerned. They are, therefore, not used.

(d) ADDITIONS TO VISCOSE

Besides the materials mentioned for controlling ripening, literally hundreds of others have been suggested or patented for addition to viscose for various purposes. These include solid and liquid, inorganic and organic compounds of almost every conceivable type, and they are added for almost every conceivable purpose, including improving or modifying the luster, dyeing, color, strength, elongation, softness, and other characteristics of the end product, and the clarity, color, surface tension, viscosity, ripening rate, and spinning characteristics of the viscose. In actual practice only a limited number of these materials are in common use and they are added mainly for securing low luster (such as titanium oxide and mineral

[71] L. Lilienfeld, U. S. Patent 980,648 (Jan. 3, 1911); *Chem. Abstracts*, **5,** 1188 (1911); Brit. Patent 14,339 (June 15, 1914); *Chem. Abstracts*, **9,** 3359 (1915); A. Bernstein, U. S. Patent 1,121,605 (Dec. 22, 1914); *Chem. Abstracts*, **9,** 377 (1915); G. A. Richter and P. C. Scherer, U. S. Patent 1,880,041 (Sept. 27, 1932); *Chem. Abstracts*, **27,** 414 (1933); H. B. Dykstra, U. S. Patent 2,072,738 (Mar. 2, 1937); *Chem. Abstracts*, **31,** 3275 (1937); Vereinigte Kunstseide-Fabriken Akt.-Ges., Brit. Patent 8742 (1908); H. Lyncke, Brit. Patent 8023 (1908); *Chem. Abstracts*, **3,** 714 (1909); Viscose Syndicate Ltd., German Patent 133,144 (Mar. 31, 1901); *Chem. Zentr.*, **73, II,** 411 (1902); Société Française de la Viscose, German Patent 187,369 (Aug. 13, 1904); *Chem. Abstracts*, **2,** 730 (1908); Continentale Viscose Compagnie, German Patent 209,161 (Oct. 20, 1903); *Chem. Abstracts*, **3,** 2223 (1909); J. P. Bemberg Akt.-Ges., German Patent 197,086 (Mar. 29, 1907); *Chem. Abstracts*, **2,** 2301 (1908); F. Becker, German Patent 234,861 (Aug. 16, 1910); *Chem. Abstracts*, **5,** 3157 (1911); Deutsche Gasglühlicht-Auer-Ges., German Patent 408,822 (Apr. 29, 1922); *Chem. Zentr.*, **96, I,** 1471 (1925); R. Linkmeyer and H. Hoyermann, German Patent 312,392 (Nov. 17, 1917); *Chem. Zentr.*, **90, IV,** 1017 (1919); F. B. Cramer, U. S. Patent 2,369,718 (Feb. 20, 1945); *Chem. Abstracts*, **39,** 3668 (1945); K. Atsuki and T. Takata, *J. Soc. Chem. Ind., Japan*, **43,** 394B (1940).

oil), for dispersing delustering agents, for controlling milkiness and spinneret incrustations, and for sponge and bottle cap (film) manufacture. Very few of the other suggested additions to viscose find any industrial application.[72]

(e) ANALYSIS OF VISCOSE

The analysis of viscose usually includes the determination of the amount of cellulose, total alkali, total sulfur, viscosity, filterability, xanthate sulfur (degree of ripeness or esterification by chemical tests), and degree of ripeness by coagulation tests.

The cellulose content of viscose may be determined readily by regeneration in the form of a film with salt solution or a mixture of salt and mineral acid. Total alkali is obtained by titration with sulfuric acid. Analysis for total sulfur is made by oxidizing the viscose with hypochlorite, hypobromite, or a mixture of hydrogen peroxide and nitric and perchloric acids, and estimating it as barium sulfate. Total sulfur may also be determined volumetrically by treating the viscose with sodium zincate and titrating the resulting zinc sulfide with iodine.[73]

Determination of apparent viscosity is carried out industrially by either the falling-ball or flow method. Although the viscometers used are of the standard types, specifications regarding size of balls, tube and capillary diameters, and other dimensions vary considerably throughout the industry. It should be understood that in view of the anomalous viscosity of viscose, flow curves relating velocity of flow to pressure are required to obtain really complete information regarding the flow characteristics of any viscose. To establish the "xanthate" viscosity of a pulp (the viscose viscosity that will be obtained as the result of a given set of process conditions), it is necessary to convert the pulp to viscose under carefully controlled conditions. The small-scale laboratory procedures for the preparation of viscose described at the beginning of this section are satisfactory for this purpose. By using the appropriate formula, data obtained by these procedures may also be employed to determine, at least approximately, the cellulose D.P.[74]

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[72] A few of the more recent patents covering additions to viscose are: J. S. Creadick, U. S. Patent 2,307,760 (Jan. 12, 1943); *Chem. Abstracts*, **37**, 3605 (1943); L. Ubbelohde, U. S. Patent 2,322,981 (June 29, 1943); *Chem. Abstracts*, **38**, 253 (1944); P. H. Schlosser, U. S. Patents 2,331,935–6 (Oct. 19, 1943); 2,362,217 (Nov. 7, 1944); *Chem. Abstracts*, **39**, 2650 (1945); 2,373,712 (Apr. 17, 1945); *Chem. Abstracts*, **39**, 4223 (1945); 2,392,103 (Jan. 1, 1946); *Chem. Abstracts*, **40**, 2984 (1946); 2,393,817 (Jan. 29, 1946); *Chem. Abstracts*, **40**, 2305 (1946); R. C. Smith, U. S. Patent 2,334,358 (Nov. 16, 1943); *Chem. Abstracts*, **38**, 2820 (1944); J. W. Hill, U. S. Patent 2,335,592 (Nov. 30, 1943); *Chem Abstracts*, **38**, 3144 (1944); J. T. Marsh, U. S. Patent 2,337,398 (Dec. 21, 1943); *Chem. Abstracts*, **38**, 3475 (1944); R. S. Bley, U. S. Patent 2,341,509 (Feb. 15, 1944); *Chem. Abstracts*, **38**, 4443 (1944); T. Koch, U. S. Patent 2,345,345 (Mar. 28, 1944); *Chem. Abstracts*, **38**, 4443 (1944); J. Nelles, U. S. Patent 2,356,079 (August 15, 1944); *Chem. Abstracts*, **39**, 199 (1945); J. E. Kirby, U. S. Patent 2,371,052 (Mar. 6, 1945); *Chem. Abstracts*, **39**, 5086 (1945); O. W. Boies, U. S. Patent 2,379,783 (July 3, 1945); *Chem. Abstracts*, **39**, 4224 (1945); H. Cowling, U. S. Patent 2,397,338 (Mar. 26, 1946); *Chem. Abstracts*, **40**, 3262 (1946); N. L. Cox, U. S. Patents 2,535,044–5 (Dec. 26, 1950); *Chem. Abstracts*, **45**, 2669, 2670 (1951); 2,536,014 (Dec. 26, 1950); *Chem. Abstracts*, **45**, 2207 (1951). See also L. Thoria, *J. Indian Chem. Soc., Ind. & News Ed.*, **11**, 63 (1948).

[73] H. L. Barthélemy and L. Williams, *Ind. Eng. Chem., Anal. Ed.*, **17**, 624 (1954).

(*1*) *Degree of Ripeness and Degree of Esterification*

Both chemical and colloidal methods are employed for determining the degree of ripeness or degree of esterification of viscose. Of the chemical methods, probably the best is the procedure based on the reaction of the xanthate with diethylchloroacetamide which converts it into an insoluble, stable derivative[30,75] whose composition is:

$$(C_6H_7O_2[OH]_x[O—CSS—CH_2—CO—N(C_2H_5)_2]_{3-x})_n$$

After precipitation of this compound, it is filtered off, and the nitrogen is determined by the Kjeldahl method. Since every nitrogen atom corresponds to one xanthate group in the original sample, this procedure gives the degree of esterification of the cellulose, and the results may be converted to xanthate sulfur.

The oldest chemical test for determining xanthate sulfur and degree of ripening is based on the reaction between cellulose xanthate and iodine which results in the formation of a so-called disulfide:

$$2\ R_{cell}OCSSNa + I_2 \xrightarrow{\qquad} R_{cell}OCSS—SSCOR_{cell} + 2\ NaI \qquad (20)$$

Because of the interference of the sulfur-containing by-products in viscose, this method is not as straightforward as the one in which diethylchloroacetamide is used, and a number of variations in procedure have been suggested.[2,22,76] However, the method is used extensively and, with suitable

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[74] G. Jayme and coworkers, *Kolloid-Z.*, **107**, 163 (1944); **108**, 20 (1944); *Melliand Textilber.*, **27**, 155 (1946).

[75] H. Fink, *Angew. Chem.*, **47**, 429 (1934).

[76] J. d'Ans and A. Jäger, *Kunstseide*, **8**, 17, 43, 57, 82, 110 (1926); *Cellulosechemie*, **16**, 22 (1935); H. Jentgen, *Laboratoriumsbuch für die Kuntseide- und Ersatzfaserstoff-Industrie*, W. Knapp, Halle (Salle), 1923, p. 55; O. Faust, E. Graumann, and E. Fischer, *Cellulosechemie*, **7**, 165 (1926); R. Bernhardt, *Kunstseide*, **8**, 164 (1926); J. Eggert, *Die Herstellung und Bearbeitung der Viscose unter bes. Berücks. d. Kunstseidefabrikation*, 2d ed., J. Springer, Berlin, 1931; G. Kita, *Kunstseide*, **8**, 221 (1926); G. de Wyss, *Ind. Eng.*

Continued on next page.

precautions, reproducible results can be obtained which agree with the diethylchloroacetamide method. Perhaps the best and simplest procedure[77] is to remove the by-product sulfur compounds by treating the viscose with acetic acid in the presence of calcium carbonate which acts as a buffer, blowing with air (or, better, oxygen-free nitrogen), and then titrating with standard iodine solution. The change in xanthate sulfur content during ripening of a representative commercial viscose is shown in Figure 74A.

The by-product sulfur content of viscose may be estimated by calculation as the difference between the total sulfur and xanthate sulfur contents. It may also be determined directly[77] by absorbing the CS_2 and H_2S, which are expelled as described in the above method for xanthate sulfur, in alcoholic NaOH and cadmium acetate solutions, respectively, and titrating with iodine.

Colloidal methods for determining the degree of esterification or ripeness of viscose are empirical in nature and measure the ease of coagulation rather than the amount of any chemical compound. They are more practical than chemical methods and they are also simpler. Two such methods are used extensively in industry as regular control methods. They involve the coagulation of viscose with sodium chloride and ammonium chloride solutions,[76,78] and are based on the fact that with increasing age viscose may be coagulated by constantly smaller amounts of electrolytes.

1. The *Salt Point* or *Salt Index Method* gives the concentration of sodium chloride solution which is *just* sufficient to coagulate a definite, small quantity of viscose which is allowed to fall into it dropwise. There are several modifications of this test. One procedure is to allow one drop of viscose to fall from the end of a small glass rod ($^3/_{16}$ in. diameter) into a 250-cc. Erlenmeyer flask containing 40 cc. of salt solution of known concentration. The solution is immediately shaken mechanically for a definite period, and the salting-out effect is noted. If the drop of viscose dissolves, the salt solution is too dilute. If it coagulates as a heavy precipitate, the solution is too concentrated. At the correct concentration of NaCl, the drop forms two or three freely suspended, "comma-shaped" particles, readily seen by the naked eye.

Chem., **17,** 1043 (1925); H. Lotze, *Kunstseide,* **16,** 290 (1934); E. Berl and H. Dillenius, *Cellulosechemie,* **13,** 1 (1932); K. Jung, *Kolloid-Z.*, **108,** 120 (1944); K. Krüger, *Kunstseide u. Zellwolle,* **25,** 370 (1947).

[77] W. H. Fock, *Kunstseide,* **17,** 117 (1935). For potentiometric titration methods for determining the by-product compounds and the degree of ripening, see R. S. Neumann and coworkers, *Cellulosechemie,* **17,** 16 (1936); P. Herrent and G. Jnoff, *J. Polymer Sci.*, **3,** 487, 834 (1948).

[78] K. Ziegler and W. Schäfer, *Cellulosechemie,* **15,** 89 (1934); V. Hottenroth, *Chem.-Ztg.*, **39,** 119 (1915); T. Mukoyama, *Kolloid-Z.*, **43,** 349 (1927); X. Herthe, *Ind. textile,* **59,** 287 (1942); E. B. Castillo, *Anales fís. y quím.* (*Madrid*), **42,** 1019 (1946); **43,** 60 (1947); F. Genert, *Kunstseide u. Zellwolle,* **23,** 80 (1941).

2. The *Ammonium Chloride* or *Hottenroth Index Method* gives the volume in cc. of a 10% NH_4Cl solution which is necessary to coagulate the viscose under certain conditions. Viscose (20 g.) is diluted with 30 cc. of water and the solution titrated with 10% NH_4Cl solution, with rapid stirring, until coagulation just sets in.

It will be noted that in the salt index method a small quantity of viscose is added to a large volume of coagulating agent. The concentration and nature of the salt solution are therefore not appreciably affected. In the ammonium chloride method, the viscose solution is in excess. Moreover, the latter method depends upon the conversion of the ammonium chloride, first, by the free NaOH in the viscose forming sodium chloride and free ammonia, and, second, by the combined sodium, forming ammonium cellulose xanthate and more sodium chloride. The ammonium chloride method is, therefore, more sensitive than the salt index method and more dependent upon the composition of the viscose. The change in salt index during ripening of a representative commercial viscose is shown in Figure 74A. It will be observed that there is a direct relationship between the salt index and xanthate sulfur curves, and hence between the colloidal and chemical methods for determining ripeness.

Other methods (including chemical, spectrochemical, physical, and colloidal) have been suggested for analyzing and examining viscose to establish its quality, the presence of insoluble matter, air, gel structure, pulp reactivity, and other properties. Among these may be mentioned filterability (which will be discussed below), microscopic examination (with dark-field illumination, under polarized light or otherwise) for gels, fibers, filtration residues, and the like, flow birefringence, and ultraviolet absorption.[4,5,57,79] With the exception of filterability and some microscopic tests these methods are not used extensively in industry.

(2) *Viscose Filterability*

The filterability of viscose is the simplest and perhaps the best measure of its quality from the point of view of xanthate and cellulose solubility, of the efficiency of the various viscose processing steps, and of the presence of insoluble matter. As mentioned above, viscose is usually subjected to several filtration steps before it can be used industrially. The first of these filtrations is by far the most important, both from a technical and economic standpoint, since it removes most of any undissolved fibers, gels, xanthate, or other impurities. Industrially, therefore, the efficiency of the first filtration step, that is, the amount of viscose which can be passed through

[79] E. Berl and H. Dillenius, *Cellulosechemie*, **13**, 1 (1932); M. Numa, *Kunstseide*, **9**, 597 (1927); C. L. Moore, *Silk and Rayon*, **8**, 563 (1934); E. Kühnel, *Kunstseide u. Zellwolle*, **21**, 369, 394 (1939); I. Jurisch, *Kunstseide u. Zellwolle*, **22**, 346 (1940); **23**, 5 (1941); K. Atsuki and T. Takata, *J. Soc. Chem. Ind., Japan*, **43**, 394B (1940); E. B. Castillo, *Ion.*, **6**, 306 (1946); F. Castellani, *Chimica e industria (Milan)*, **28**, 6 (1946); E. Schauenstein and E. Treiber, *Melliand Textilber.*, **32**, 43 (1951).

these filters before plugging, is a direct reflection of the viscose quality. Analytically, viscose filterability can be determined in the laboratory by a number of procedures which are useful not only for plant control purposes but for predicting the behavior of raw materials, for determining the effect of other variables in viscose manufacture and for determining the reactivity of pulps to NaOH and/or CS_2. All of these procedures involve the preparation of viscose under a standard set of conditions and passing it through a suitable standard filtering apparatus under fixed conditions of pressure, temperature, time, and filter medium. Depending upon the type of data obtained, filterability may be reported in various terms. Among these may be mentioned[80]:

(1) The amount of viscose filtered in a given time, such as 60 min.

(2) The actual plugging value—the amount of viscose actually required to plug the filter by carrying the test to complete plugging.

(3) The calculated plugging value: (a) the amount of viscose obtained by determining the rate of filtration at intervals such as 5, 10, 15, and 30 min., plotting the rates against the corresponding total amounts filtered, drawing the best straight line through the points, and extrapolating to zero rate; or, (b) plugging value:

$$(G) = \frac{2(P_2 + P_1)}{2 - P_2/P_1}$$

(4) Plugging constant:

$$(K_w) = 100{,}000 \times \frac{2 - P_2/P_1}{P_1 + P_2}$$

where P_1 = grams of viscose filtered from 0 to 20 min. and P_2 = grams of viscose filtered from 20 to 60 min.

Most of the factors affecting filtration have already been mentioned. It is beyond the scope of this Section to discuss the subject in any detail except to say that bad filtration is usually the result of slime, gels, fibers, and other incompletely dissolved fiber components, the causes of which are varied and numerous. The type (e.g., morphology, D.P., and native fiber structure) of pulp, impurities (organic and inorganic) in raw materials, carbon disulfide concentration, viscose composition, and every step in the processing of viscose are all vital in achieving good solubility and a good filtering solution.[4,5,80,81] (For the effect of some viscose processing factors on filterability, see Figures 71 and 73.)

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[80] L. H. Smith, editor, *Synthetic Fiber Developments in Germany*, Textile Research Institute, New York, 1946, p. 195. For theoretical considerations involved, including criticism of some of these formulas see: P. H. Hermans and H. L. Bredée, *Rec. trav. chim.*, **54**, 680 (1935); T. Bergek and T. Ouchterlony, *Svensk Papperstidn.*, **49**, 470 (1946); P. H. Teunissen, *Svensk Papperstidn.*, **51**, 497 (1948); H. L. Vosters, *Svensk Papperstidn.*, **53**, 29, 613, 771 (1950); V. E. Gonsalves, *Rec. trav. chim.*, **69**, 873 (1950); A. Matthes, *Chem. Tech.* (Berlin), **3**, 13 (1951).

(f) COAGULATION AND REGENERATION

In view of the fact that viscose is of interest solely as an intermediate product from which the dissolved cellulose may be recovered in some desired physical form, its most important reaction is that by which the regeneration of the cellulose is brought about *rapidly*. The spontaneous decomposition of the xanthate during ripening obviously occurs too slowly to be of use industrially for this purpose, and the reaction with neutral salts results only in coagulation, with the xanthate remaining unchanged. Mineral acids and acid salts, however, decompose the xanthate *directly*, causing both coagulation and regeneration of the cellulose.[82] At the same time, the free alkali is neutralized and the by-product salts are decomposed with liberation of CS_2, H_2S, CO_2, and free sulfur. The main reactions, as occurring with sulfuric acid, may be represented as follows:

$$2\ R_{cell}OCSSNa + H_2SO_4 \longrightarrow 2\ R_{cell}OH + Na_2SO_4 + 2\ CS_2 \qquad (21)$$

$$2\ NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O \qquad (22)$$

$$Na_2CS_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S + CS_2 \qquad (23)$$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O \qquad (24)$$

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S \qquad (25)$$

If sodium sulfite is present in the viscose, liberation of H_2S is prevented and colloidal sulfur formed instead:

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2 \qquad (26)$$

$$SO_2 + 2H_2S \longrightarrow 2\ H_2O + 3S \qquad (27)$$

With few exceptions, these reactions, combined with the coagulation effect of neutral salts, are the basis of all industrial uses of viscose. The viscose is either extruded into a bath containing mineral acid plus one or more salts causing immediate and simultaneous coagulation and regenera-

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[81] A. Marschall, *Kunstseide u. Zellwolle*, **24,** 188 (1942); O. Samuelson, *Svensk Papperstidn.*, **48,** 517 (1945); **52,** 448, 465 (1949); *Svensk Kem. Tid.*, **61,** 227 (1949); T. Kleinert and V. Mössmer, *Österr. Chem.-Ztg.*, **51,** 29 (1950); H. A. Wannow, *Reyon, Synthetica, Zellwolle*, **29,** 135 (1950).

[82] Cellulose xanthate may also be decomposed by electrophoresis, the regenerated cellulose depositing at the anode. See P. Karrer and T. Lieser, *Cellulosechemie*, **7,** 3 (1926).

tion, or it is partially coagulated and regenerated in an acid–salt bath followed by completion of the reaction by a second acid–salt bath or other treatment, or it is first just coagulated in a solution of one or more salts followed by regeneration in a second bath containing mineral acid.[83] The first two "one-bath" and "two-bath" systems are used most widely for the manufacture of filaments, whereas the latter "two-bath" system is employed mostly in the production of film structures.[84] Regardless of the regenerating methods employed, the cellulose is obtained as hydrated or mercerized cellulose, the characteristics of which have already been described in Chapter IV-D.

(*1*) *Technical Applications*[7]

In the production of filaments (rayon and staple fiber), the viscose is forced under pressure through very fine holes contained in cup-shaped nozzles (spinnerets) immersed in a coagulating bath. The emerging viscose filaments are coagulated immediately, and the coagulated fibers from each spinneret (each spinneret contains a number of holes) are combined into a main thread which is simultaneously drawn through the bath, stretched, and collected on a suitable take-up device. The size of the main thread, in the case of continuous filament rayon, varies from about 40 to 2200 denier, the number of filaments per thread varying from about 14 to 960. In the production of staple fiber, the number of holes per spinneret is much greater, in some cases several thousand, and the size of the main thread, per spinneret, may be as high as 10,000 denier or even higher.

Three methods are used in rayon production for collecting the freshly spun threads. They may be (1) wound on a rotating spool or bobbin, in the "spool" or "bobbin" process; or (2) collected in the form of a "cake" by centrifugal force in a revolving bucket, in the "bucket" or "pot" spinning process[85]; or (3) they may be wound on a specially designed rotating reel or other thread storage device which receives and then advances the thread automatically and continuously, to a series of other similar reels

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[83] For example, see F. L. Durr, *Rayon Textile Monthly*, **27**, 126, 196, 246, 300, 357, 414 (1946).

[84] Dry spinning methods have also been suggested but they have not been applied industrially. See H. Hoffmann, *Papier-Fabr.*, **39**, 14 (1941); R. O. Herzog and H. Hoffmann, U. S. Patent 2,036,752 (Apr. 7, 1936); *Chem. Abstracts*, **30**, 3645 (1936); J. L. Costa, U. S. Patent 2,317,152 (Apr. 20, 1943); *Chem. Abstracts*, **37**, 5867 (1943); L. Paulus, Swedish Patent 116,135 (Apr. 2, 1946)..

[85] C. P. Walker, *Rayon and Synthetic Textiles*, **31**, No. 12, 34 (1950); *Silk and Rayon*, **21**, 1386 (1947); A. J. Hall, *Fibres*, **9**, 19 (1948).

(as in the Industrial Rayon Corporation[86] "continuous" spinning and purification process) or along a single pair of canted rollers (as in the recently developed Nelson, American Viscose Corporation, and Kohorn processes[87]).

After spinning, and when coagulation of the viscose is complete (regeneration of the cellulose may or may not be complete), the yarn is subjected to a number of operations, including stretching, washing, desulfuring, bleaching, finishing or oiling, drying, twisting, and winding to suitable packages (e.g., skeins, cones, tubes). These operations vary considerably throughout the industry, although in the "spool" and "pot" spinning processes they are all discontinuous. Each spool or cake, representing 0.50 to 2.0 lb. of rayon, is treated individually as such, and the whole operation, from spinning to the final drying of the yarn, requires from one to six days. In the Industrial Rayon Corporation "continuous" process, all of these operations except the final coning step are continuous; each thread is carried forward individually over a series of thread-advancing reels from the moment of extrusion until it is completely processed, dried, twisted, and wound on bobbins, and all of the operations are accomplished in about 6 min. (see Fig. 75). So far as is known, the other "continuous" processes are restricted mainly to the production of rayon for tires and no desulfuring, bleaching, or twisting steps are included.

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[86] T. R. Olive, *Chem. & Met. Eng.*, **45,** 668 (1938); *Silk and Rayon*, **20,** 1298 (1946); **21,** 1386 (1947); J. V. and S. L. Sherman, *The New Fibers*, Van Nostrand, New York, 1946, pp. 222–5.

[87] *Rayon Textile Monthly*, **28,** 633 (1947); A. J. Hall, *Fibres*, **9,** 62, 107 (1948); S. W. Barker, U. S. Patents 2,525,760 and 2,526,110 (Oct. 17, 1950); *Chem. Zentr.*, **122, II,** 2825 (1951); R. W. Stanley, U. S. Patents 2,516,157 (July 25, 1950); 2,532,465 (Dec. 5, 1950); 2,582,293 (Jan. 15, 1952); J. W. Coleman and coworkers, U. S. Patent 2,536,093 (Jan. 2, 1951); *J. Textile Inst.*, **42,** A286 (1951); H. J. McDermott and J. W. Pedlow, U. S. Patent 2,536,094 (Jan. 2, 1951); *J. Textile Inst.*, **42,** A286 (1951); *Rayon and Synthetic Textiles*, **32,** No. 11, 9 (1951); H. Von Kohorn, Australian Patent Application No. 29,713/49, filed Sept. 7, 1949.

Many other schemes for the continuous spinning and purification of rayon have been proposed but none of them appear to be in use industrially. See: F. L. Durr, *Rayon Textile Monthly*, **28,** 468 (1947); S. W. Barker and R. Alleston, *J. Textile Inst.*, **39,** P1 (1948); P. W. Frisk, *Rayon and Synthetic Textiles*, **30,** No. 9, 49 (1949); A. J. L. Moritz, U. S. Patents 2,302,792 (Nov. 24, 1942); *Chem. Abstracts*, **37,** 2577 (1943); 2,346,696 (Apr. 18, 1944); *Chem. Abstracts*, **38,** 6094 (1944); A. L. Ewing, U. S. Patents 2,317,747 (Apr. 27, 1943); *Chem. Abstracts*, **37,** 6140 (1943); 2,435,430 (Feb. 3, 1948); J. H. Truesdail, U. S. Patents 2,333,278–9 (Nov. 2, 1943); *Chem. Abstracts*, **38,** 2510 (1944); W. E. Neff, U. S. Patent 2,340,611 (Feb. 1, 1944); C. F. Gram, U. S. Patent 2,319,812 (May 25, 1943); *Chem. Abstracts*, **37,** 6459 (1943); H. O. Naumann, U. S. Patent 2,476,757 (July 19, 1949); G. A. M. Heim, U. S. Patent 2,334,325 (Nov. 16, 1943); *Chem. Abstr.*, **38,** 2820 (1944); F. A. J. van Hall, U. S. Patent 2,539,980 (Jan. 30, 1951); *J. Textile Inst.*, **42,** A287 (1951); R. Levison, U. S. Patents 2,566,455–6–7 (Sept. 4, 1951); H. A. Kuljian, U. S. Patents 2,495,936 (Jan. 31, 1950); 2,501,776 (Mar. 28, 1950); 2,504,703 (Apr. 18, 1950); and many others.

Excess coagulating bath is first removed from the freshly spun yarn by washing with water, sometimes in the presence of small amounts of an alkaline agent such as ammonia or sodium bicarbonate. (Carbon disulfide recovery is sometimes carried out at this point.) In the "spool" and "pot" spinning processes, the yarn may be dried after this washing step,

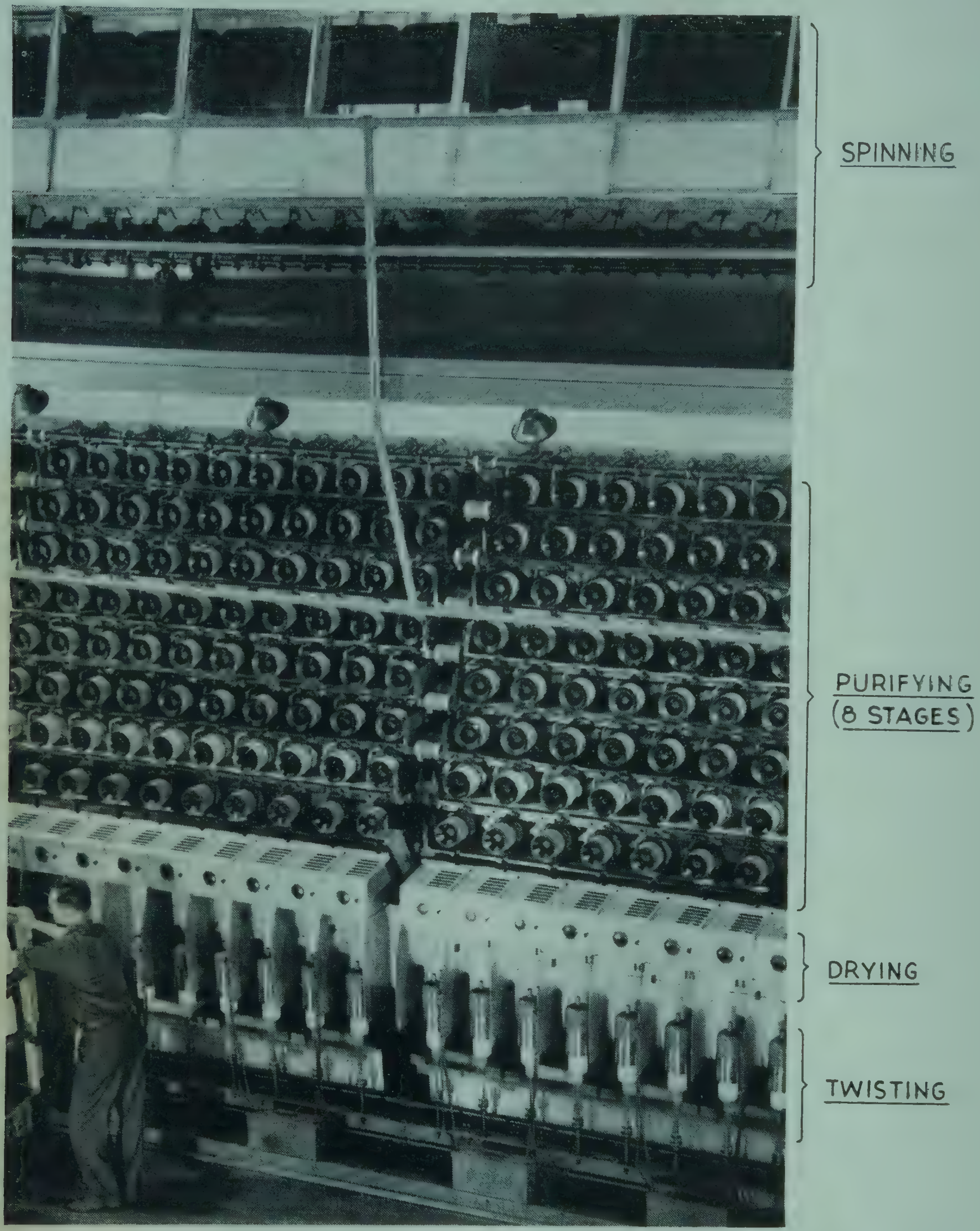

Fig. 75. A continuous spinning and processing machine. This view shows how rayon is spun, purified, finished, dried, and twisted in synchronized operation. Courtesy of Industrial Rayon Corporation.

or further treated directly in the "gel" state (as is, or after reeling to skeins). Sulfur, which is always present, probably in both free and combined forms, is then removed by treatment with a dilute (0.5–1.5%) solution of sodium sulfide, ammonium sulfide, sodium hydroxide, or sodium carbonate.[88] Other desulfuring agents have also been proposed.[89] When bleaching is required, it follows the desulfuring operation and is usually carried out with sodium hypochlorite solution[90] containing about 0.05% available chlorine. After desulfuring and bleaching, the yarn may receive other treatments such as finishing, sizing, and tinting, after which it is dried. The latter operation, which is extremely important in establishing the properties of the final product, may be carried out with or without tension, depending upon whether or not the yarn is to possess any residual shrinkage. In any case, the tension during drying must be uniform to minimize any residual shrinkage differences.

The manufacture of rayon staple resembles that of continuous filament rayon except that the main threads are much larger, as already pointed out, and the spinning and purification operations are nearly always continuous. Two main processes are in use, depending upon the cutting operation: (1) The filaments may be cut into staple immediately after spinning or washing and the remaining operations carried out on the cut fibers or (2) the thread or rope from a number of spinnerets may be combined and processed in rope form, after which it is cut to the desired length and then dried.[91]

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[88] L. A. Paley, U. S. Patent 1,779,103 (Oct. 21, 1930); *Chem. Abstracts*, **25**, 205 (1931); H. H. Parker, U. S. Patent 1,931,266 (Oct. 17, 1933); *Chem. Abstracts*, **28**, 321 (1934); H. B. Kline, U. S. Patent 1,932,789 (Oct. 31, 1933); *Chem. Abstracts*, **28**, 659 (1934).

[89] P. C. Scherer, *Ind. Eng. Chem.*, **25**, 1319 (1933); A. D. Conley and E. C. Stillwell, U. S. Patent 1,371,300 (Mar. 15, 1921); *Chem. Abstracts*, **15**, 1812 (1921); E. K. Gladding and T. S. Sharpe, U. S. Patent 1,655,097 (Jan. 3, 1928); *Chem. Abstracts*, **22**, 1050 (1928); A. Hartmann and J. Uytenbogaart, U. S. Patent 2,194,470 (Mar. 26, 1940); *Chem. Abstracts*, **34**, 4924 (1940); I. G. Farbenindustrie Akt.-Ges., Brit. Patent 279,437 (Oct. 14, 1927); *Chem. Abstracts*, **22**, 2847 (1928); A. E. Stein, Brit. Patents 428,955 (May 22, 1935); 429,165 (May 24, 1935); J. G. Evans, Brit. Patent 464,116 (Apr. 9, 1937); *Chem. Abstracts*, **31**, 6463 (1937); Herminghaus & Co., French Patent 655,729 (June 14, 1928); *Chem. Abstracts*, **23**, 4072 (1929).

[90] See also J. S. Fonda and G. W. Filson, U. S. Patent 2,064,300 (Dec. 15, 1936); *Chem. Abstracts*, **31**, 889 (1937); R. O. Denyes, U. S. Patent 2,479,605 (Aug. 23, 1949); *Chem. Abstracts*, **44**, 840 (1950); J. W. Jacokes, U. S. Patent 2,488,667 (Nov. 22, 1949); *Chem. Abstracts*, **44**, 7068 (1950).

[91] For example, see: O. Von Kohorn, U. S. Patent 2,308,576 (Jan. 19, 1943); *Chem. Abstracts*, **37**, 3952 (1943); L. E. Lovett, U. S. Patent 2,315,265 (Mar. 30, 1943).

In the production of cellophane, viscose is forced under pressure (cast) through a slit in a suitable hopper which is immersed in a coagulating bath. As the viscose emerges from the slit, it is coagulated at once in the form of a thin, wide sheet or film. This is led by means of suitable rollers through a series of baths in which, after regeneration of the cellulose is complete, the film is washed, desulfured, bleached, etc., and finally dried. The entire operation is continuous, the machine being somewhat similar to, although much smaller than, a paper machine.[92]

Sausage casings, bands, and similar structures are made by extruding viscose through an annular slot immersed in a suitable coagulating bath. The viscose is coagulated in the form of a tube, which is processed on a continuous machine through the various purification and drying steps.[93] Bottle caps, bands, and the like may be formed by covering suitable mandrels with a film of viscose by dipping, and then immersing them in a coagulating medium. The viscose is thus regenerated as a film in the form of the particular mandrel used, after which the structure is removed from the mandrel and subjected to the necessary purification operations. Other cellulose structures are made from viscose in an analogous manner.[94]

(2) *Coagulating Baths and the Spinning Operation*

Since viscose is used most widely in the production of rayon and staple fiber, its coagulation and regeneration are of concern mostly from the viewpoint of filament formation, that is, spinning.[95] In this connection, the composition of the coagulating bath (the importance of raw materials, viscose composition, viscosity, degree of ripening, and other factors have already been mentioned) is a prime consideration. The bath serves several functions. It must coagulate the cellulose dispersed in the viscose and decompose the remaining xanthate, at least in part; it must also neutralize the free alkali, decompose the by-product salts, and be compatible with the by-products of the reaction. Moreover, it must coagulate and regenerate the viscose as a homogeneous plastic mass, at a suitable speed so that the coagulated filaments may be readily and continuously led through the bath, stretched to a considerable extent if desired, and collected, all without interruption. These results have been achieved most satisfactorily by combining a reagent which actively decomposes the xanthate (dilute mineral acid) with an agent which simply coagulates (a salt).[96] The so-called Müller bath,[97] consisting of dilute sulfuric acid combined with a soluble sulfate salt, represents such a combination, and baths of this general type, although considerably modified, are in general use throughout the industry. The composition used is normally in the range of 7 to 13% H_2SO_4 and 13 to 25% Na_2SO_4. $MgSO_4$ or $(NH_4)_2SO_4$[98] is sometimes used in place of all or part of the Na_2SO_4. In addition, most coagulating baths today contain small amounts (0.5–2.0%) of $ZnSO_4$[99] and, in some cases, also organic materials like glucose[100] and wetting or dispersing agents.[101]

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[92] J. E. Brandenberger, U. S. Patents 1,548,864 (Aug. 11, 1925); *Chem. Abstracts,* **19,** 3018 (1925); 1,601,289 (Sept. 28, 1926); *Chem. Abstracts,* **20,** 3814 (1926).

[93] W. P. Cohoe, U. S. Patent 1,163,740 (Dec. 14, 1915).

[94] For example, see: G. Pum and A. Glaessner, U. S. Patent 1,142,619 (June 8, 1915); *Chem. Abstracts,* **9,** 1978 (1915); L. Mostny, U. S. Patent 1,611,056 (Dec. 14, 1926); *Chem. Abstracts,* **21,** 321 (1927).

[95] H. Erbring, *Kolloid-Beihefte,* **44,** 171 (1936); R. Klaus, *Kunstseide,* **15,** 9 (1933); **16,** 148 (1934); A. Wehrung, *Cellulosechemie,* **11,** 170 (1930); N. Matsumoto, *J. Soc. Chem. Ind., Japan,* **41,** B380 (1938); R. Inoue, *J. Soc. Chem. Ind., Japan,* **41,** B334, B357 (1938); **42,** B18 (1939); F. H. Müller, *Physik. Z.,* **42,** 123 (1941); P. H. Hermans, *Physics and Chemistry of Cellulose Fibres,* Elsevier, The Netherlands, 1949; *J. Polymer Sci.,* **1,** 389, 393 (1946); **2,** 632 (1947); **3,** 1 (1948); R. Gaebel, *Kunstseide u. Zellwolle,* **27,** 153 (1949); J. Müller, *Kunstseide u. Zellwolle,* **28,** 385 (1950); H. L. Vosters, *Svensk Papperstidn.,* **53,** 59 (1950).

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[96] For some early bath compositions see: C. F. Cross, E. J. Bevan, and C. Beadle, U. S. Patent 604,206 (May 17, 1898); C. H. Stearn, U. S. Patents 622,087 (Mar. 28, 1899); 716,778 (Dec. 23, 1902); 725,016 (Apr. 7, 1903); Brit. Patent 2,529 (1902).

[97] F. Steimmig, *Kunstseide*, **12**, 242 (1930); M. Müller, U. S. Patent 836,452 (Nov. 20, 1906); Vereinigte Glanzstoff-Fabriken Akt.-Ges., German Patents 187,947 (Apr. 2, 1905); 287,955 (Feb. 15, 1912); *Chem. Abstracts*, **10**, 2145 (1916).

[98] T. H. Verhave, U. S. Patent 1,280,338 (Oct. 1, 1918); *Chem. Abstracts*, **12**, 2695 (1918); J. C. Hartogs, German Patent 324,433 (Mar. 1, 1914); *Chem. Zentr.*, **91, IV**, 486 (1920).

[99] S. S. Napper, U. S. Patent 1,045,731 (Nov. 26, 1912); *Chem. Abstracts*, **7**, 706 (1913); F. C. Niederhauser and H. B. Kline, U. S. Patent 1,661,574 (Mar. 6, 1928); *Chem. Abstracts*, **22**, 1483 (1928); J. J. Stöckly and A. Brötz, U. S. Patent 2,015,201 (Sept. 24, 1935); *Chem. Abstracts*, **29**, 7657 (1935); Vereinigte Glanzstoff-Fabriken Akt.-Ges., German Patent 260,479 (Sept. 16, 1911); *Chem. Abstracts*, **7**, 3236 (1913).

[100] L. P. Wilson, U. S. Patent 970,589 (Sept. 20, 1910); *Chem. Abstracts*, **4**, 3298 (1910); E. Bronnert, U. S. Patent 1,426,953 (Aug. 22, 1922); *Chem. Abstracts*, **16**, 3763 (1922); Vereinigte Glanzstoff-Fabriken Akt.-Ges., German Patent 240,846 (Sept. 26, 1908); *Chem. Abstracts*, **6**, 2169 (1912).

[101] J. J. Polak and J. G. Weeldenburg, U. S. Patent 2,125,031 (July 26, 1938); *Chem. Abstracts*, **32**, 7725 (1938); L. Rose, U. S. Patent 2,302,589 (Nov. 17, 1942); *Chem. Abstracts*, **37**, 2500 (1943); R. S. Bley, U. S. Patents 2,310,207–8 (Feb. 9, 1943); *Chem. Abstracts*, **37**, 4247, 4248 (1943); 2,345,570 (Apr. 4, 1944); *Chem. Abstracts*, **38**, 4444 (1944); 2,348,203 (May 9, 1944); *Chem. Abstracts*, **39**, 1291 (1945); B. W. Collins, U. S. Patents 2,359,749–50 (Oct. 10, 1944); *Chem. Abstracts*, **39**, 3933, 1052 (1945); 2,519,227 (Aug. 15, 1950); *Chem. Abstracts*, **44**, 11111 (1950); H. B. Kline, U. S. Patents 2,394,519 (Feb. 5, 1946); *Chem. Abstracts*, **40**, 2628 (1946); 2,422,021 (June 10, 1947); *Chem. Abstracts*, **41**, 5721 (1947); D. E. Drew, U. S. Patent 2,360,405 (Oct. 17, 1944); *Chem.*

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Of the hundreds of reagents which have been studied for spinning baths, perhaps the most important are those in the class of inorganic salts. The coagulating effect of sodium and ammonium salts has been mentioned. Heavy-metal salts also react with and coagulate viscose to give the corresponding metal xanthates.[2,102] Since yarn properties (such as strength, elongation, dye affinity, luster, softness, and cross section) vary with the nature and concentration of the salt, many of them have become of definite interest as spinning bath constituents.

The action of salts is due in part to changes in pH,[43,103] to changes in the speed of regeneration (which is reduced by the addition of salts[104]), and to the hydration of the ions. Most important, however, is the dehydrating, salting-out action which is common to all salts. In this connection the valence law of colloid chemistry and the Hofmeister series apply,[105] but only in part, in view of the hydrophilic character of viscose and the chemical reactions (mentioned above) which occur simultaneously. Thus, ammonium salts have a greater coagulating power than sodium salts, whereas the coagulating effect of divalent Mg^{++} is of the same order as monovalent Na^{+}, and heavy-metal salts like Zn^{++}, Fe^{++}, and Ni^{++} are several hundred times more effective than either Na^{+} or Mg^{++}.[106] The retardative influence on regeneration shown by these cations is in about

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Abstracts, **39**, 1538 (1945); A. Cresswell, U. S. Patent 2,442,331 (June 1, 1948); *Chem. Abstracts*, **42**, 6114 (1948); T. A. H. Blaas, U. S. Patent 2,451,148 (Oct. 12, 1948); *Chem. Abstracts*, **43**, 850 (1949); S. A. Moss, Jr., U. S. Patent 2,489,310 (Nov. 29, 1949); *Chem. Abstracts*, **44**, 7062 (1950); K. R. Brown, U. S. Patent 2,495,833 (Jan. 31, 1950); *Chem. Abstracts*, **44**, 10320 (1950).

[102] Many of these heavy-metal xanthates are highly colored compounds. For example, the lead salt is carmine red; the copper salt, chocolate brown; the iron salt, brownish red; the nickel salt, cherry red; the zinc salt, white; the mercury salt, yellow; the cobalt salt, brownish black; the bismuth salt, red-brown; the cadmium salt, yellow; the silver salt, rose-brown; the antimony salt, red-yellow. Since solutions of pure xanthate do not give such intensely colored precipitates and since the compounds can also be obtained from the reaction products of CS_2 and NaOH, they are probably only in part cellulose xanthate salts. See H. Seidel, *Mitt. Tech. Gewerb.-Mus. Wien*, **10**, 35 (1900); R. Wolffenstein and E. Oeser, *Kunstseide*, **7**, 29 (1925); T. Lieser, *Cellulosechemie*, **10**, 156 (1929).

[103] K. Tanemura, *Cellulose Ind.* (Tokyo), **11**, 12, 100 (1935).

[104] C. L. Moore, *Silk and Rayon*, **9**, 19 (1935); S. Hase, *J. Soc. Chem. Ind., Japan*, **35**, Suppl. binding, 367 (1932).

[105] E. Berl and H. Dillenius, *Cellulosechemie*, **13**, 1 (1932); K. Leuchs, *Chem.-Ztg.*, **47**, 801 (1923).

[106] L. Mirlas, *Cellulosechemie*, **16**, 37 (1935); M. Horio, *Textile Research J.*, **20**, 373 (1950); D. Vermaas and J. J. Hermans, *Rec. trav. chim.*, **67**, 983 (1948).

the same order as their coagulating power,[107] and, when two or more of them are combined, their activity is usually greater than the sum of the individual salts.

These characteristics explain the use of various salts in baths and the special interest in zinc and other polyvalent cations (with zinc sulfate, for example, a relatively stable film containing zinc cellulose xanthate is formed on the surface of the filaments), particularly in stretch-spinning processes to permit the application of tension, to increase strength, and to produce fine filament yarns. $MgSO_4$, being more soluble than Na_2SO_4, permits higher salt concentrations in the bath without crystallization difficulties, whereas $ZnSO_4$, even in the small concentrations mentioned above, deepens dyeing and improves strength, softness, and luster. Further very significant effects along these and other lines are obtained by higher concentrations (2.5–30.0%) of $ZnSO_4$,[108] and other salts, including the sulfates[109] of aluminum, chromium, iron, arsenic, nickel, cobalt, and manganese, have been proposed for various specific purposes. Sodium bisulfite, sodium and ammonium phosphates, sodium borate, sodium thiosulfate, sodium and ammonium bicarbonates, sodium silicate, sodium salts of fatty acids, sodium benzene sulfonate, salts of certain organic bases, and others[110] have also been suggested for use.

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[107] V. Duchesnoy, *Russa*, **9**, 641 (1934); A. Pakshver and coworkers, *Trans. Inst. Chem. Technol. Ivanovo (U. S. S. R.)*, **1940**, No. 3, 178.

[108] W. P. Dreaper, U. S. Patent 1,626,454 (Apr. 26, 1927); *Chem. Abstracts*, **21**, 2063 (1927); Brit. Patent 239,254 (May 2, 1924); *Chem. Abstracts*, **20**, 2079 (1926); R. Picard, U. S. Patent 1,831,030 (Nov. 10, 1931); *Chem. Abstracts*, **26**, 844 (1932); I. P. Davis, U. S. Patent 2,114,915 (Apr. 19, 1938); *Chem. Abstracts*, **32**, 4784 (1938); J. H. Givens, H. W. Biddulph, and L. Rose, U. S. Patent 2,192,074 (Feb. 27, 1940); *Chem. Abstracts*, **34**, 4569 (1940); N. L. Cox, U. S. Patents 2,535,044–5 (Dec. 26, 1950); *Chem. Abstracts*, **45**, 2669, 2670 (1951).

[109] C. H. Stearn, U. S. Patent 725,016 (Apr. 7, 1903); J. C. Hartogs, U. S. Patent 1,573,062 (Feb. 16, 1926); *Chem. Abstracts*, **20**, 1328 (1926); I. P. Davis, U. S. Patent 2,114,915 (Apr. 19, 1938); *Chem. Abstracts*, **32**, 4784 (1938); C. H. Stearn and C. F. Topham, Brit. Patent 16,604 (July 28, 1903); *J. Soc. Chem. Ind.*, **23**, 784 (1904); H. Kizu and K. Kadowaki, *J. Soc. Chem. Ind., Japan*, **38**, Suppl. binding, 195 (1935); J. J. Stöckly, U. S. Patents 2,315,559–60 (Apr. 6, 1943); *Chem. Abstracts*, **37**, 5590 (1943); N. L. Cox, U. S. Patents 2,347,883–4 (May 2, 1944); *Chem. Abstracts*, **39**, 192 (1945); 2,364,273 (Dec. 5, 1944); *Chem. Abstracts*, **39**, 3668 (1945); E. B. Castillo, *Rev. acad. cienc. exactas, fís.-quím. y nat. Zaragoza*, [2], **3**, No. 1, 33 (1948).

[110] C. N. Waite, U. S. Patents 759,332 (May 10, 1904); 816,404 (Mar. 27, 1906); C. A. Ernst, U. S. Patents 798,027 (Aug. 22, 1905); 792,888 (June 20, 1905); E. Bronnert, U. S. Patents 1,102,237 (July 7, 1914); *Chem. Abstracts*, **8**, 2947 (1914); 1,374,718 (Apr. 12, 1921); *Chem. Abstracts*, **15**, 2730 (1921); 1,376,672 (May 3, 1921); *Chem. Abstracts*, **15**, 2730 (1921); 1,387,882 (Aug. 16, 1921); *Chem. Abstracts*, **15**, 4053 (1921);

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The nature of the acid is important also.[111] Although sulfuric acid is perhaps the only acid used commercially, others[112] have been proposed, such as acetic and other fatty acids, hydrochloric, nitric, benzenesulfonic, phosphoric, and arsenic acids.

Many organic compounds[113] have been investigated as constituents of spinning baths, but few are actually used. For the most part, organic additions are of interest in influencing thread formation apart from coagulation and regeneration. The outstanding materials of this type are glucose and certain wetting or dispersing agents. Glucose is used rather widely in concentrations of 2 to 10%, mainly to prevent crystallization. It also suppresses the action of the acid and the oxidation of H_2S, and influences the continuity of spinning, softness, and other yarn properties.[100] Various wetting and dispersing agents are used in the bath (in relatively low concentrations) in some plants to prevent or reduce the formation of deposits in the spinneret holes.[101] These deposits, representing insoluble by-products of the reaction between viscose and spinning bath, adversely affect the quality of the thread and the continuity of spinning. They may be controlled under ordinary conditions by proper attention to various spinning factors, but the production of very fine filament yarns and the use of higher spinning speeds and of certain bath compositions to permit high stretching have aggravated this condition in recent years, creating interest in new and novel methods of correction.[114]

C. F. Cross, U. S. Patent 1,538,689 (May 19, 1925); *Chem. Abstracts*, **19**, 2136 (1925); H. Chavassieu, U. S. Patent 2,034,711 (Mar. 24, 1936); *Chem. Abstracts*, **30**, 3256 (1936); S. Peessarer, Brit. Patent 16,583 (Aug. 15, 1905); W. F. Underwood, U. S. Patent 2,413,123 (Dec. 24, 1946).

[111] Y. Kami and M. Nozaki, *Cellulose Ind.* (Tokyo), **5**, 117 (1929); O. Faust, *Ber.*, **62B**, 2567 (1929).

[112] C. A. Ernst, U. S. Patent 792,888 (June 20, 1905); C. H. Stearn, U. S. Patent 725,016 (Apr. 7, 1903); L. P. Wilson, U. S. Patent 970,589 (Sept. 20, 1910); *Chem. Abstracts*, **4**, 3298 (1910); E. Bronnert, U. S. Patents 1,102,237 (July 7, 1914); *Chem. Abstracts*, **8**, 2947 (1914); 1,376,672 (May 3, 1921); *Chem. Abstracts*, **15**, 2730 (1921); 1,464,805 (Aug. 14, 1923); *Chem. Abstracts*, **17**, 3259 (1923); J. C. Hartogs, U. S. Patent 1,534,382 (Apr. 21, 1925); *Chem. Abstracts*, **19**, 1781 (1925); L. Lilienfeld, U. S. Patent 1,881,740 (Oct. 11, 1932); *Chem. Abstracts*, **27**, 601 (1933).

[113] C. A. Ernst, U. S. Patent 792,888 (June 20, 1905); M. T. Callimachi, U. S. Patent 1,449,380 (Mar. 27, 1923); *Chem. Abstracts*, **17**, 1888 (1923); F. C. Niederhauser and A. E. Sunderland, U. S. Patent 1,625,562 (Apr. 19, 1927); *Chem. Abstracts*, **21**, 2063 (1927).

[114] R. Soukup, U. S. Patent 2,324,437 (July 13, 1943); *Chem. Abstracts*, **38**, 253 (1944); I. F. Walker, U. S. Patent 2,364,407 (Dec. 5, 1944); *Chem. Abstracts*, **39**, 4223 (1945); G. H. White, U. S. Patent 2,394,957 (Feb. 12, 1946); *Chem. Abstracts*, **40**, 2627 (1946); A. Cresswell, U. S. Patent 2,515,697 (July 18, 1950); *Chem. Abstracts*, **44**, 9674 (1950); A. Wehrung, *Kunstseide u. Zellwolle*, **28**, 84 (1950).

Although coagulation and regeneration usually occur simultaneously, they do not occur at the same rate. The absolute concentrations and the ratio of acid and salts [104,115] determine which of these reactions predominates and, in turn, the shrinkage characteristics of the gel and the quality and characteristics of the final yarn. In this connection, the presence of various materials in small amounts as impurities, such as traces of metals, may have a profound effect on the spinning operation. The cross section of the filaments, which is indicative of the initial shrinkage and of many yarn properties, also varies characteristically with bath (and viscose) composition.[116] "High-swelling" baths, such as neutral salt solutions or concentrated sulfuric acid alone, give a circular cross section, with a relatively smooth outline and little, if any, "skin." "Low-swelling" conditions, produced, for example, by acid baths with high salt concentrations and high degrees of xanthate substitution, cause the initial formation of a semipermeable surface film or "skin"; the lower the swelling is, the thicker is the skin. As coagulation and regeneration progress, an exosmosis of water takes place from the interior to the exterior of the filament, causing a decrease in volume and, hence, a shrinkage of the surface film, and giving an irregular, crenulated cross section. Although considerable information has been developed[117] as to the actual mechanism of "skin" formation as well as to the relationship and orientation of the "skin" and "core" and the irregularity of cross sections of viscose filaments, these phenomena are still not completely understood.

Besides the chemical composition of the bath, a number of physical factors play important roles in the spinning operation. These include bath temperature (the rates of the reactions involved increase with temperature), bath travel, spinneret composition, spinning speed, spinning tension, and stretch. All of these factors[118] as well as viscose and bath composition are interdependent, so that it is nearly always impossible to change any one

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[115] P. Martin, *Rusta-Rayonne*, **11**, 275 (1936); E. Bronnert, U. S. Patent 1,393,197 (Oct. 11, 1921); *Chem. Abstracts*, **16**, 837 (1922); and other Bronnert patents; P. Thivet, *Rusta-Rayonne*, **11**, 401 (1936).

[116] E. Bronnert, *J. Soc. Dyers Colourists*, **38**, 153 (1922); R. O. Herzog, *Leipzig Monatschr. Textile-Ind.*, **41**, 352 (1926); A. Jäger, *Kunstseide*, **13**, 325 (1931); P. A. Koch, *Klepzig's Textil-Z.*, **40**, 17, 284 (1937).

[117] J. M. Preston, *J. Soc. Chem. Ind.*, **50**, 199T (1931); *J. Textile Inst.*, **40**, T327 (1949); F. F. Morehead and W. A. Sisson, *Textile Research J.*, **15**, 443 (1945); W. Schramek and E. Zehmisch, *Kolloid-Beihefte*, **48**, 93 (1938); K. Wuhrmann, *Helv. Chim. Acta*, **28**, 666 (1945).

[118] Y. Mitugi and coworkers, *J. Soc. Chem. Ind., Japan*, **46**, 944 (1943); R. Prince and J. Seiberlich, *J. Phys. Chem.*, **50**, 222 (1946).

of them without also making compensating changes in others. Bath temperature is usually controlled in the range of 45 to 55°C. where one-bath systems are employed, and the bath travel may vary from about 10 in. to several hundred inches. Spinnerets are made mostly of precious metals, high-platinum alloys being preferred.[119] Spinning speed varies considerably, depending upon such factors as type of spinning machine, filament size, and bath composition. Most operations today employ speeds in the range of 3000 to 4000 in. per minute, although considerable attention is being given to faster operation.[120] Speeds up to 10,000 in. per minute and even higher are possible, although they involve radical changes from present practice.

The tension–stretch relationships during spinning are vitally important from the viewpoint of fiber properties. In the viscose, the cellulose particles are dispersed at random, although it may be that the chains are more or less straightened and parallel to each other. In the spinning operation, alignment of the particles (orientation) occurs as a basic process accompanying or following coagulation, regeneration, and the initial gel shrinkage; the degree of orientation determines in part the strength, elongation, dyeing, and other characteristics of the fiber. Some orientation of the particles on the outside of the filaments is brought about by surface friction as the viscose passes through the spinneret holes. The major orienting effect, however, is accomplished by a stretch imparted to the filaments due to the fact that the velocity of collection of the filaments is always greater than the extrusion.

The total stretch for any given yarn is governed by the spinneret hole diameter, which varies with different producers and with the filament size from 0.0020 in. for the finest filaments to about 0.0060 in. for the coarsest. The *effect* of the stretch depends upon the stage at which it is applied. In the early methods of spinning "without tension" in which the thread passes directly from spinneret to collecting device, the stretch is imparted almost exclusively close to the spinneret where the filament is still in a "fluid" state. This gives little orientation and the fibers are characterized by low tenacity and high elongation. Present methods, for the most part, involve so-called "tension spinning" or "stretch spinning" practices[121] in which at least part of the total stretch occurs relatively farther from the spinneret, that is, later in the coagulation–regeneration cycle. This is accomplished by interposing various mechanical "braking" devices[122] (such as fixed guides, freely rotating guides, and positively driven rollers) between the spinneret and the final collecting device. Although these stretching procedures are most commonly used in conjunction with baths of the Müller type, highest breaking strengths are obtained when they are combined with special bath compositions such as strong (50–86%) sulfuric acid[123] (which imparts a simultaneous coagulating, swelling, and plasticizing effect) or with Müller-type baths followed by secondary baths or treatments, usually at higher temperatures.[124] By thus delaying the

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[119] For example, see R. V. Williams and E. R. McKee, U. S. Patent 2,135,611 (Nov. 8, 1938); *Chem. Abstracts*, **33**, 1496 (1939); H. Whitehead, U. S. Patent 2,334,890 (Nov. 23, 1943); *Chem. Abstracts*, **38**, 2820 (1944). For spinneret hole design see H. J. Jones, U. S. Patent 2,341,555 (Feb. 15, 1944); *Chem. Abstracts*, **38**, 4444 (1944).

[120] H. Jentgen, *Kunstseide*, **19**, 261 (1937); R. Soukup, U. S. Patents 2,307,863–4 (Jan. 12, 1943); *Chem. Abstracts*, **37**, 3606 (1943); F. R. Millhiser, U. S. Patent 2,440,057 (Apr. 20, 1948); *Chem. Abstracts*, **42**, 4364 (1948); N. Drisch and R. Prion, U. S. Patent 2,511,699 (June 13, 1950); *Chem. Zentr.*, **122**, **I**, 544 (1951); J. W. Pedlow and coworkers, U. S. Patent 2,510,135 (June 6, 1950).

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[121] O. Faust, *Kunstseide*, **14**, 362 (1932).

[122] C. A. Ernst, U. S. Patent 808,148 (Dec. 26, 1905); W. Harrison, U. S. Patent 1,930,803 (Oct. 17, 1933); *Chem. Abstracts*, **28**, 321 (1934); H. Pfannenstiel and H. Meyer, U. S. Patent 1,933,999 (Nov. 7, 1933); *Chem. Abstracts*, **28**, 640 (1934); F. H. Griffin, U. S. Patent 1,950,922 (Mar. 13, 1934); *Chem. Abstracts*, **28**, 3586 (1934); H. A. Schrenk, U. S. Patent 1,968,912 (Aug. 7, 1934); *Chem. Abstracts*, **28**, 6310 (1934); W. H. Bradshaw, U. S. Patent 2,012,984 (Sept. 3, 1935); *Chem. Abstracts*, **29**, 7075 (1935); W. H. Bradshaw and G. P. Hoff, U. S. Patents 2,083,251–2 (June 8, 1937); *Chem. Abstracts*, **31**, 5579 (1937); B. Borzykowski, Brit. Patent 149,295 (Aug. 31, 1917); A. J. L. Moritz, U. S. Patent 2,302,971 (Nov. 24, 1942); *Chem. Abstracts*, **37**, 2577 (1943); J. W. Coleman and coworkers, U. S. Patent 2,536,093 (Jan. 2, 1951); *J. Textile Inst.*, **42**, A286 (1951).

[123] These baths have apparently not been commercially satisfactory. See L. Lilienfeld, U. S. Patent 1,683,199 (Sept. 4, 1928); *Chem. Abstracts*, **22**, 3990 (1928); and other patents of Lilienfeld.

[124] H. C. Stuhlmann, U. S. Patent 1,901,007 (Mar. 14, 1933); *Chem. Abstracts*, **27**, 3075 (1933); A. Bernstein, U. S. Patent 1,996,989 (Apr. 9, 1935); *Chem. Abstracts*, **29**, 3513 (1935); I. P. Davis, U. S. Patent 2,114,915 (Apr. 19, 1938); *Chem. Abstracts*, **32**, 4784 (1938); J. H. Givens, H. W. Biddulph, and L. Rose, U. S. Patent 2,192,074 (Feb. 27, 1940); *Chem. Abstracts*, **34**, 4569 (1940); A. Hartmann and J. Uytenbogaart, U. S. Patent 2,194,470 (Mar. 26, 1940); *Chem. Abstracts*, **34**, 4924 (1940); Zellstofffabrik Waldhof and A. Bernstein, Brit. Patent 335,605 (June 27, 1929); *Chem. Abstracts*, **25**, 1672 (1931); Châtillon (Soc. anon. italiana per la seta artificiale), Brit. Patent 370,943 (Jan. 13, 1931); *Chem. Abstracts*, **27**, 3088 (1933); S. Riko, Y. Akizuki, and Y. Kikuti, *J. Soc. Chem. Ind., Japan*, **39**, Suppl. binding, 31 (1936); I. P. Davis, U. S. Patent 2,312,152 (Feb. 23, 1943); *Chem. Abstracts*, **37**, 4899 (1943); H. Fink, U. S. Patent 2,327,516 (Aug. 24, 1943); *Chem. Abstracts*, **38**, 865 (1944); G. I. Thurmond, U. S. Patents 2,328,307 (Aug. 31, 1943); *Chem. Abstracts*, **38**, 865 (1944); 2,369,190–1 (Feb. 13, 1945); *Chem. Abstracts*, **39**, 5488 (1945); A. S. Brown, U. S. Patent 2,433,733 (Dec. 30, 1947); *Chem. Abstracts*, **42**, 2114 (1948); E. A. Tippetts, U. S. Patent 2,439,829 (Apr. 20, 1948); H. W. Swank, U. S. Patent 2,440,226 (Apr. 20, 1948); G. M. A. Kayser, U. S. Patent 2,452,130 (Oct. 26, 1948); *Chem. Abstracts*, **43**, 1990 (1949); F. R. Millhiser, U. S.

Continued on next page.

stretching, orientation of the interior of the filaments as well as of the surface occurs, and, hence, higher tenacity results. (The higher tenacity is obtained, however, at the expense of elongation.) Whereas the older spinning methods, "without tension," give breaking strengths of the order of 1.6 g. per denier (31,000 lb. per sq. in.), "stretch spinning" methods are now common which give 2.5 to 4.25 g. per denier, and, experimentally, strengths as high as 6.0 g. per denier (117,000 lb. per sq. in.) have been obtained.

Space does not permit further discussion of the spinning operation (filament formation) or of the extrusion of viscose for the production of films and the like. Much of the investigational work on the subject is covered by References 84–124, inclusive, but it should be made clear that the processes involved are extremely complicated and still require considerable study for their complete elucidation.

After completion of the spinning operation (i.e., coagulation, regeneration, and orientation), there is little if any change in the basic structure or characteristics of the gel filaments during the steps of washing, desulfuring, or bleaching. In the drying operation, however, the final shrinkage of the gel structure takes place. Drying conditions (such as temperature, rate, uniformity, and amount of tension) therefore are extremely important in determining the final structure and hence the properties (dyeing, tensile strength, elongation, residual shrinkage, etc.) of the final product.

(g) FURTHER REACTIONS OF VISCOSE

Viscose undergoes several other reactions not mentioned in the previous discussion. For example, xanthic esters may be formed according to the general reaction:

$$\mathrm{R_{cell}OCSSNa + X{-}R \longrightarrow R_{cell}OCSSR + NaX} \qquad (28)$$

in which R is an organic radical and X the negative ion of an inorganic acid. Thus methyl iodide forms methyl cellulose xanthate,[125] and diethyl sulfate forms ethyl cellulose xanthate. Both of these compounds are soluble in alkali and in certain organic solvents, and may be spun or formed into plastic masses.

Patent 2,453,332 (Nov. 9, 1948); J. A. Calhoun, Jr., U. S. Patent 2,484,012 (Oct. 11, 1949); *Chem. Abstracts*, **44**, 1714 (1950); M. Horio and S. Nagata, *J. Soc. Chem. Ind., Japan*, **46**, Suppl. binding, 155B (1943); W. Schramek, *Melliand Textilber.*, **28**, 420 (1947).

[125] L. Lilienfeld, U. S. Patent 1,680,224 (Aug. 7, 1928); *Chem. Abstracts*, **22**, 3777 (1928); Brit. Patent 252,654 (Oct. 18, 1926); *Chem. Abstracts*, **21**, 2384 (1927); German Patent 519,138 (May 30, 1926); *Chem. Abstracts*, **25**, 2847 (1931).

When cellulose xanthate or viscose is allowed to react with halogen derivatives of polyvalent alcohols like α-dichlorohydrin, or with halogen derivatives of anhydrides of polyvalent alcohols such as epichlorohydrin, or with trithiocarbonic acid esters of polyvalent alcohols, one or more of the OH groups of the cellulose is replaced[126] and compounds useful for spinning into filaments and the like are produced.

With halogenated fatty acids, salts, and esters, viscose forms cellulose xantho fatty acid derivatives.[30,127] With monochloroacetic acid, for example, the reaction is:

$$\mathrm{R_{cell}OCSSNa + ClCH_2COONa \longrightarrow \underset{\text{Sodium salt of cellulose xanthoacetic acid}}{R_{cell}OCSSCH_2COONa} + NaCl} \qquad (29)$$

The xantho fatty acid derivative thus formed may react further with ammonia, or with organic amines, such as aniline,[128] as follows:

$$\mathrm{R_{cell}OCSSCH_2COONa + C_6H_5NH_2 \longrightarrow \underset{\substack{\text{Cellulose}\\ \text{phenylthiourethan}\\ \text{Cellulose}\\ \text{xanthoanilide}}}{R_{cell}OCSNHC_6H_5} + \underset{\substack{\text{Sodium}\\ \text{thioglycolate}}}{CH_2(SH)COONa}} \qquad (30)$$

If the salt of the above thiourethan is now treated with an ester of an inorganic acid, such as ethyl iodide, the corresponding ethyl ester of cellulose phenylthiourethan results.[129]

Cellulose xanthate, itself, also reacts with organic amines[130] forming N-substituted thiourethans of the type:

$$\mathrm{R_{cell}OCSNHR}$$

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[126] L. Lilienfeld, U. S. Patents 1,938,032 (Dec. 5, 1933); *Chem. Abstracts*, **28**, 1188 (1934); 2,004,876 (June 11, 1935); *Chem. Abstracts*, **29**, 5285 (1935); 2,021,862–4 (Nov. 19, 1935); *Chem. Abstracts*, **30**, 614 (1936); see also L. Lilienfeld, Brit. Patents 335,906 (Mar. 25, 1929); *Chem. Abstracts*, **25**, 1995 (1931); 335,993–4 (Mar. 25, 1929); 356,286 (Mar. 10, 1930); *Chem. Abstracts*, **26**, 5756 (1932).

[127] T. Nakashima, *J. Soc. Chem. Ind., Japan*, **31**, Suppl. binding, 31 (1928); L. Lilienfeld, U. S. Patent 1,642,587 (Sept. 13, 1927); *Chem. Abstracts*, **21**, 3742 (1927); Brit. Patents 231,800 (Nov. 23, 1925); *Chem. Abstracts*, **19**, 3592 (1925); 341,843 (June 20, 1929); *Chem. Abstracts*, **25**, 4125 (1931).

[128] L. Lilienfeld, U. S. Patents 1,674,401 (June 19, 1928); *Chem. Abstracts*, **22**, 2839 (1928); 1,674,405 (June 19, 1928); *Chem. Abstracts*, **22**, 2840 (1928); 1,906,910 (May 2, 1933); *Chem. Abstracts*, **27**, 3605 (1933); Brit. Patent 231,802 (May 22, 1924).

[129] L. Lilienfeld, U. S. Patent 1,674,402 (June 19, 1928); *Chem. Abstracts*, **22**, 2839 (1928).

[130] L. Lilienfeld, U. S. Patent 1,881,741 (Oct. 11, 1932); *Chem. Abstracts*, **27**, 601 (1933).

If the cellulose xanthoacetic acid, mentioned above, is dissolved in methylaniline,[131] a salt, cellulose xanthoacetic acid amine, is formed:

$$R_{cell}OCSSCH_2COOH{\cdot}HN(CH_3)C_6H_5$$

Xanthates of hydroxyalkyl derivatives of cellulose are obtained from the reaction of cellulose with a cyclic ether of a polyhydric alcohol and then treating the resultant compound with carbon disulfide and alkali.[132]

Diazomethane converts the xanthate to monomethyl dicellulose:

$$[C_6H_7O_2(OH)_{2.5}(OCH_3)_{0.5}]_n$$

Diazonium compounds[133] also react with cellulose xanthate according to the equation:

$$R_{cell}OCSSNa + ClN{=}NR \longrightarrow R_{cell}OCSSN{=}NR + NaCl \longrightarrow R_{cell}OCSSR + N_2 \quad (31)$$

in which R represents an aromatic nucleus such as C_6H_5.

On treatment with acrylonitrile, cellulose xanthate (in viscose) is readily converted to cellulose cyanoethyl ether which, in the presence of the NaOH in the viscose, then hydrolyzes with the formation of the sodium salt of cellulose carboxyethyl ether:

$$R_{cell}OCSSNa + CH_2{=}CHCN \longrightarrow R_{cell}OCH_2CH_2CN \longrightarrow R_{cell}OCH_2CH_2COONa \quad (32)$$

The cyanoethyl ether may be isolated as such, or the reaction mixture may be used directly for spinning modified rayons.[134]

The reaction of viscose with iodine has been described. The light-yellow disulfide formed here is insoluble and quite stable, although it is converted back to the normal cellulose xanthate by sodium amalgam.[41] Still other xanthates of cellulose, and other reactions of ordinary cellulose xanthate, as well as mixtures of cellulose xanthate and cellulose ethers, are possible.[135]

[131] L. Lilienfeld, U. S. Patent 1,890,393 (Dec. 6, 1932); *Chem. Abstracts*, **27**, 1718 (1933).

[132] L. Lilienfeld, U. S. Patents 1,910,440 (May 23, 1933); *Chem. Abstracts*, **27**, 4080 (1933); 2,306,451 (Dec. 29, 1942); *Chem. Abstracts*, **37**, 3270 (1943).

[133] J. H. Helberger, German Patent 562,180 (Oct. 1, 1931); *Chem. Abstracts*, **27**, 841 (1933).

[134] J. P. Hollihan and S. A. Moss, Jr., *Ind. Eng. Chem.*, **39**, 929 (1947); J. A. Somers, *Brit. Rayon and Silk J.*, **26**, No. 312, 62 (1950).

[135] L. Lilienfeld, U. S. Patents 2,051,051 (Aug. 18, 1936); *Chem. Abstracts*, **30**, 6943 (1936); 2,052,478 (Aug. 25, 1936); *Chem. Abstracts*, **30**, 7341 (1936); 2,100,010 (Nov. 23, 1937); *Chem. Abstracts*, **32**, 779 (1938); 2,163,607 (June 27, 1939); *Chem. Abstracts*, **33**, 8013 (1939); 2,169,207 (Aug. 8, 1939); *Chem. Abstracts*, **33**, 9641 (1939); 2,176,085 (Oct. 17, 1939); *Chem. Abstracts*, **34**, 1172 (1940); 2,176,799 (Oct. 17, 1939); *Chem. Abstracts*, **34**, 1173 (1940).

G. DEGRADATION OF CELLULOSE DERIVATIVES

L. F. McBurney

The susceptibility of cellulose derivatives to degradative processes is a reflection both of the chemical nature of the cellulose chain molecule and of that of the substituents along the chain. The extent to which each of these factors contributes to the total effect is dependent upon the type and degree of substitution of the individual polymer. For convenience of discussion it is desirable to group the derivatives into two broad classifications.

A satisfactory segregation of the common cellulose derivatives can be based on their solubility either in aqueous or in nonaqueous media, as is apparent from a consideration of their solubility properties. The water-soluble derivatives, in the main, are much less completely substituted than are the organosoluble types. As a result, the stability of the water-soluble types is less dependent upon the chemical nature of the substituent and is more nearly comparable to that of the parent cellulose. The stability of the organosoluble types, on the other hand, is influenced primarily by the chemical nature of the substituent and to a much lesser extent by the cellulose backbone. Both classes, however, are subject to a solvent interaction which also plays a part in stability. This effect is more pronounced with the organosoluble types since a wide variety of solvents or plasticizers are employed in their use as coatings or plastics.

Both water-soluble and organosoluble cellulose derivatives will undergo degradation by hydrolytic, oxidative, and microbiological processes. The relative ease with which this deterioration occurs will vary widely, not only between the two classes of compounds but also between different members of the same class; for example, although both organosoluble ethyl cellulose and cellulose acetate are susceptible to oxidative degradation by atmospheric oxygen, cellulose acetate will be perfectly stable at temperatures where ethyl cellulose shows a rapid breakdown. The deterioration of cellulose derivatives usually manifests itself by a loss in viscosity with a corresponding loss of tensile strength, the formation of color, and in many cases marked changes in solubility properties.

The stability of the water-soluble cellulosics will be discussed first in this section with their susceptibility to microbiological, hydrolytic, and oxidative degradation being considered in that order. These derivatives have achieved commercial importance comparatively recently and, as a result, information dealing with their susceptibility to deterioration is very incomplete. The order of presentation has been chosen since it represents both the importance and level of knowledge of the degradative process involved. The water-soluble cellulosics which have reached commercial importance today are all ethers of degrees of substitution of two or less; thus this discussion will serve as a brief introduction to the subject of ether stability in general.

Solvent-soluble cellulosics, in direct contrast to their water-soluble counterparts, have been utilized for years, and a very considerable literature has been accumulated in reference to their stability. With these more highly substituted derivatives, oxidation by molecular oxygen is by far the most important single degradative reaction for both organic ethers and esters, with hydrolytic breakdown occupying a secondary role, and thermal degradation being important only in the case of the inorganic ester, cellulose nitrate. The portion of this discussion devoted to organic-soluble cellulosics will, therefore, emphasize and attempt to interpret primarily the processes involved in the oxidative degradation reaction and less attention will be paid to the other causes of instability with the exception of the thermal breakdown of cellulose nitrate.

1. Water-Soluble Cellulose Derivatives

The water-soluble cellulose derivatives, such as the sodium salt of carboxymethyl cellulose, are finding an increasing commercial utilization in the food, pharmaceutical, textile, and adhesive industries, where hydrophilic colloids with suspending, thickening, stabilizing, and film-forming properties are required. These materials are quite stable to storage in the dry state; in solution, however, they will undergo deterioration. The major source of this degradation has been shown to be the attack by a number of genera of bacteria and fungi of widespread occurrence in nature. Similar deterioration can result from hydrolytic or oxidative attack.

(a) MICROBIOLOGICAL DEGRADATION

The growth of microorganisms in solutions of these water-soluble derivatives produces a variety of undesirable properties; namely, liquefaction, cloudiness, discoloration, and odor.[1] It is believed that the enzyme which hydrolyzes the 1,4-glucosidic linkage in carboxymethyl cellulose is identical with that responsible for similar attack in cellulose (see Chapter III-C-5). The ease of attack by these microorganisms appears to be independent of degree of polymerization (D.P.) but to be quite sensitive to the degree of substitution (D.S.) of the material.[2]

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[1] G. G. Freeman, A J. Baillie, and C. A. Macinnes, *Chemistry & Industry*, **1948,** 279.

The effect of degree of substitution on ease of enzymatic hydrolysis of carboxymethyl cellulose is illustrated in Figure 76 from which it is apparent that those samples containing one or more carboxymethyl groups per anhydroglucose unit are quite resistant to attack, whereas those containing unsubstituted units in the cellulose chains will be readily degraded. Evidence of this type is responsible for the conclusion that the degrading enzyme is the same as that which brings about cellulose degradation and is capable of utilizing only the unsubstituted glucose residues. Commercial carboxymethyl celluloses have degrees of substitution below one, and thus their solutions are susceptible to such attack.

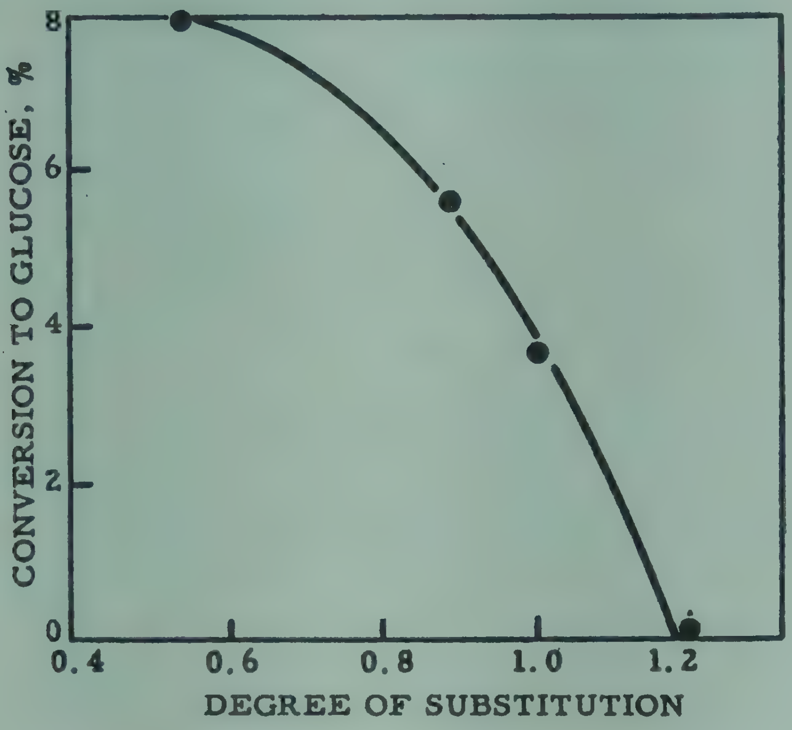

Fig. 76. Effect of degree of substitution of sodium carboxymethyl cellulose on extent of enzymatic hydrolysis to glucose (Reese, Siu, and Levinson[2]). Samples were hydrolyzed with filtrates of *Aspergillus fumigatus* cultures for 2 hrs. at 50°C.

Two general methods are available for control of microbiological degradation: One is the use of heat sterilization; the other is the use of bacteriostats. The effectiveness of the latter reagents (with cellulose derivatives) can be seen from Table 43 where samples of sodium carboxymethyl cellulose treated with *m*-cresol and monochloro-3,5-xylenol are compared with an untreated sample. The data in Table 43 illustrate the fact that microbiological degradation can be readily controlled and need not be a detrimental factor in solution use of water-soluble cellulosics.

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[2] E. T. Reese, R. G. H. Siu, and H. S. Levinson, *J. Bacteriol.*, 59, 485 (1950).

TABLE 43

Bacteriostatic Action of *m*-Cresol and Monochloro-3,5-xylenol in 2% Solutions of Sodium Carboxymethyl Cellulose in Aqueous Sulfate Medium (Freeman, Baillie, and Macinnes[1])

	No bacteriostat	*m*-Cresol		Monochloro-3,5-xylenol	
		0.1%	0.2%	0.1%	0.2%
Viscosity at 20°C., centistokes					
Initially	67	60	72	72	68
After 10-day incubation	8	52	60	60	56
Bacterial count per ml.					
Initially	500	100	100	100	100
After 2 days	250,000	—	—	—	—
After 3 days	50,000,000	100	100	100	100
After 7 days	50,000,000	80,000	80,000	100	100
After 10 days	200,000,000	100,000	100,000	4,000	1000
pH after 10 days	6.6	8.3	9.0	7.2	6.8
Final appearance of solutions	H_2S present FeS precipitated	No change	No change	No change	No change

(b) HYDROLYTIC DEGRADATION

The sensitivity of water-soluble cellulose derivatives to acid hydrolysis is closely analogous to that of cellulose itself (see Chapter III-C). It differs only in that physical structure, which is the controlling factor in cellulose hydrolysis, has little effect on the water-soluble derivatives since they are reasonably well dispersed in solution and have lost the characteristic fiber structure. Reduction in degree of polymerization is frequently accompanied by a reduction in degree of substitution.[3,4] In most cases the chain-cleavage reaction is much more rapid than is the loss of substituent from the ether because of the greater reactivity of the glucosidic (acetal) type of bond in comparison to the normal ether bond.

The parallelism which exists between the acid hydrolysis of cellulose and that of its water-soluble derivatives has been clearly demonstrated by Gibbons[5] in his studies on methyl cellulose. This work established that

[3] A. Pacault, M. Bouttemy, and O. Tanaevsky, *Bull. soc. chim. France*, **1952**, 345.

[4] T. E. Timell, *Svensk Papperstidn.*, **56**, 245 (1953).

[5] G. C. Gibbons, *J. Textile Inst.*, **43**, T25 (1952).

the activation energy of the hydrolysis was independent of the degree of substitution and the concentration of the hydrolyzing acid and had a value of 30,150 cal. The activation energies reported for the hydrolysis of cellulose solutions in concentrated acids are in the same range, being 29,800 cal. in 51% sulfuric acid[6] and 27,260 and 29,600 cal. in phosphoric acid.[6,7]

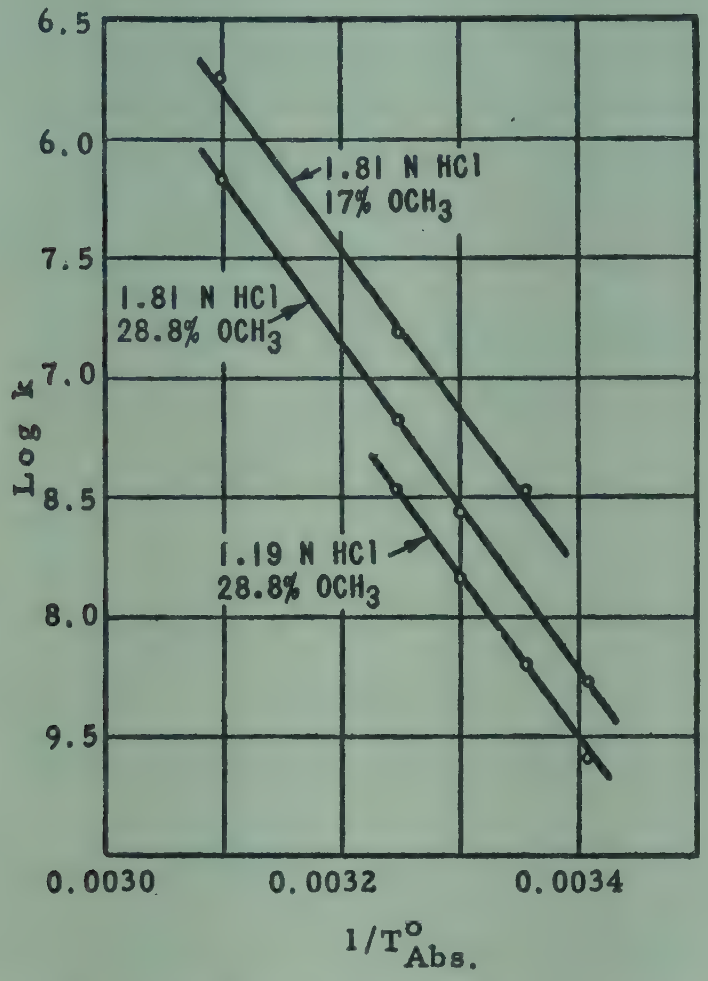

Fig. 77. Arrhenius plots for hydrolysis of methyl celluloses in HCl (Gibbons[5]). The slopes of the straight lines obtained by plotting the logarithm of the experimentally determined reaction rate constant k against the reciprocal of the absolute temperature T all give an activation energy E of 30,150 cal. for the hydrolysis reaction.

The data in Figure 77 show the constancy of the Arrhenius plot obtained from two methyl celluloses of different D.S. and show as well the effect of different acid concentrations. The uniformity of the slopes of the curves shows the same reaction to be occurring in all cases. These same data illustrate the dependence of the rate of reaction on the degree of substitution, from which it can be concluded that the rate of hydrolysis decreases as the degree of substitution is increased.

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[6] K. Freudenberg, W. Kuhn, W. Dürr, F. Bolz, and G. Steinbrunn, *Ber.*, **63B**, 1510 (1930); K. Freudenberg and G. Blomqvist, *Ber.*, **68B**, 2070 (1935).

[7] G. V. Schulz and H. J. Löhmann, *J. prakt. Chem.*, **157**, 238 (1941).

De-etherification of cellulose ethers can be accomplished by treatment with hot concentrated mineral acids. More dilute acids or treatment with concentrated acids at room temperature have generally been considered only to attack the glucosidic chain bonds and to leave the substituent ether linkage untouched. Pacault, Bouttemy, and Tanaevsky[3] have reported that sulfuric acid solutions in concentration above 5 *N* will bring about the de-etherification of carboxymethyl cellulose at room temperature as shown in Figure 78. The loss of ether groups is accompanied by a very considerable change in viscosity as shown in Figure 79.

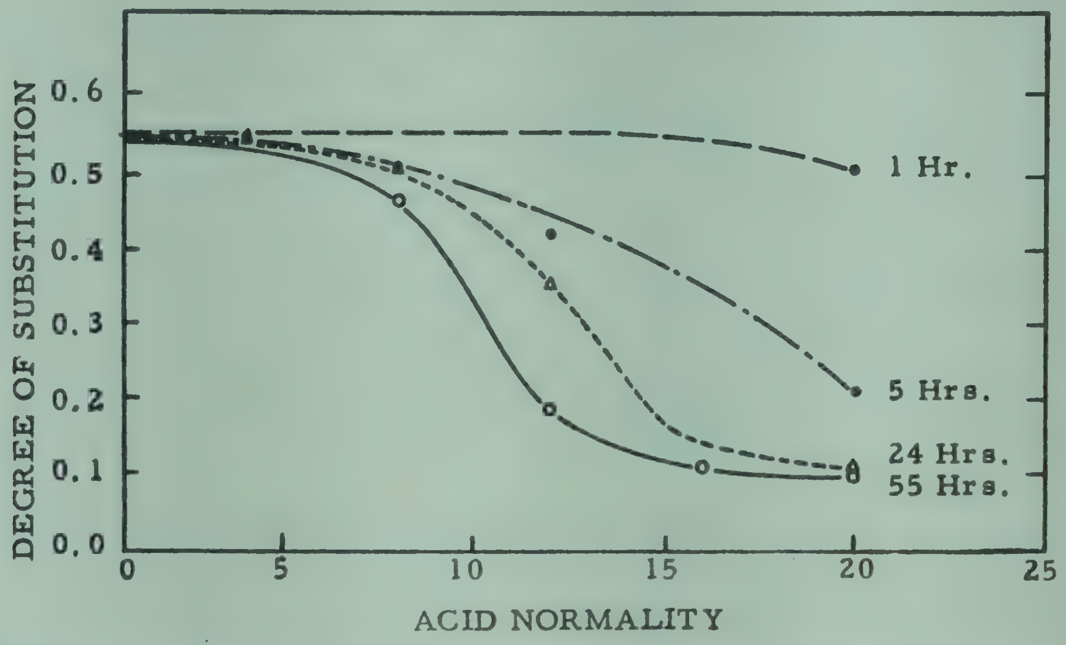

Fig. 78. De-etherification of sodium carboxymethyl cellulose (original D.S. = 0.55) on contact with aqueous sulfuric acid solutions at room temperature for various lengths of time (Pacault, Bouttemy, and Tanaevsky[3]).

Timell[4] has reinvestigated this de-etherification phenomena because of its important implications which would invalidate many conclusions relating to the substituent distributions in water-soluble cellulose derivatives. It is the conclusion from Timell's work that the measured change in D.S. is the result of excessive destruction of the amorphous regions of the cellulose fibers, which are also more highly substituted with carboxymethyl groups. These areas are rendered soluble and are lost during the washing process. Thus the undissolved residue will have a reduced D.S. but the loss is the result of chain cleavage and not of de-etherification.

The acid lability of the cellulose chain is an inherent property of its chemical structure, and there is no magic inhibitor or retarder which can be added to overcome its breakdown. The chain cleavage of the water-soluble derivatives can be minimized by careful control of the pH of the solution, either by maintaining the solutions slightly on the alkaline side or by the use of buffer salts to control the acidity at or near the neutral point. Storage of acidic aqueous solutions of cellulosics will invariably result in a loss in viscosity which will increase with the acidity of the solution.

(c) OXIDATIVE DEGRADATION

The end uses of water-soluble derivatives, up to the present time, are such that behavior of these derivatives toward conditions favorable to oxidative breakdown has been relatively unimportant. The literature, as a result, contains no information bearing on their so-called weathering stability which includes the effects of elevated temperatures, high alkali concentration, air, and ultraviolet light, conditions which normally lead to oxidative instability in high polymers. Under the influence of these reagents, Steurer and Mertens[8] have shown the organosoluble methyl celluloses to degrade, and similar effects have been found with the higher substituted ethyl celluloses, which will be discussed under the organosoluble derivatives. Cellulose itself is unstable to air and alkali, as shown previously (see Chapter III-C). These facts lead to the conclusion that the water-soluble derivatives also would be labile. The ease of this reaction and extent to which it will occur remain at present as a relatively unexplored field of cellulose chemistry which, as new uses for the water-soluble gums are found, will undoubtedly become of major importance.

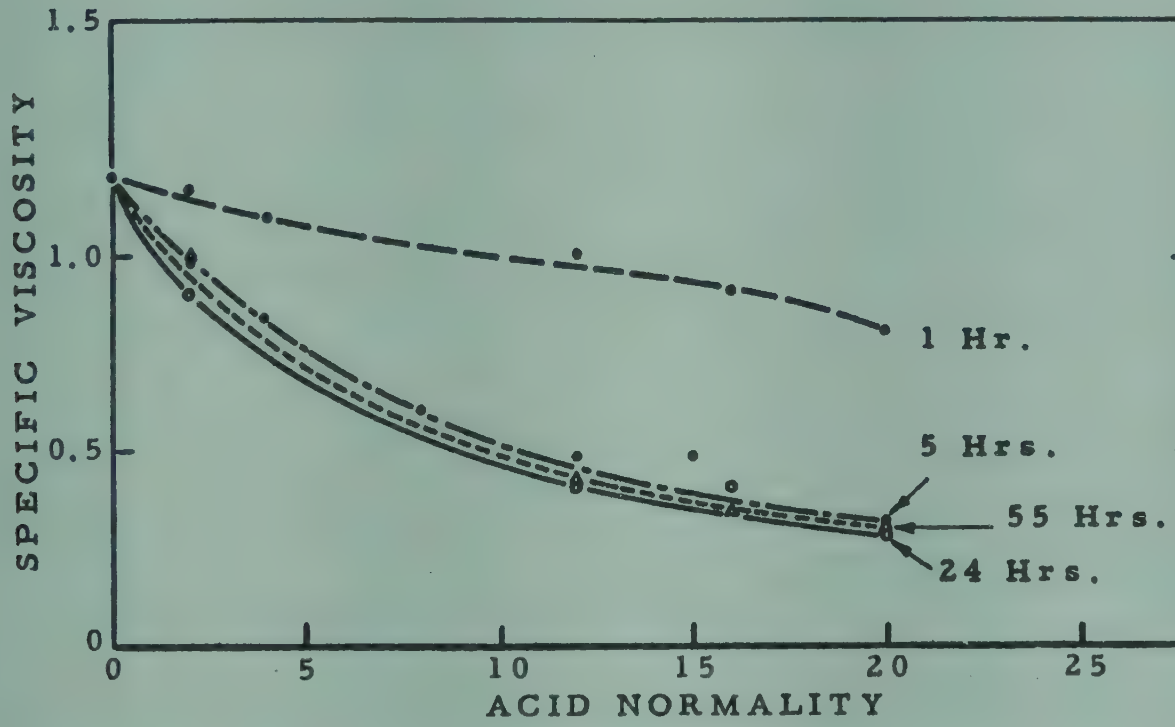

Fig. 79. Decrease in specific viscosity of sodium carboxymethyl cellulose on contact with aqueous sulfuric acid solutions at room temperature for various lengths of time (Pacault, Bouttemy, and Tanaevsky[3]).

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[8] E. Steurer and H.-W. Mertens, *Ber.*, **74B**, 790 (1941).

2. Organosoluble Cellulose Derivatives

The industrial utilization of organosoluble cellulose derivatives as protective coatings, films, plastics, and fibers requires them to be resistant to a wide spectrum of degradative processes. The most critical specification which they are called upon to meet is the ability to withstand outdoor weathering conditions. Under such exposure the cellulose derivatives are subjected to varying degrees of heat, light, moisture, and oxygen, all of which are capable of bringing about severe deterioration. The result of these degradative environmental processes can be lumped together under the general heading of oxidative instability. Since the various derivatives differ in their general susceptibility to these factors, they will be discussed individually.

(a) CELLULOSE ETHERS

The principal organosoluble cellulose ether, from the commercial viewpoint, is ethyl cellulose, the derivative which has therefore received the most intensive investigation. Benzyl cellulose was utilized in Europe for a time but is no longer of commercial importance. The discussion of the oxidative degradation of ethyl cellulose will apply equally well to the benzyl ether; the latter, however, is much more sensitive to oxidation.

(*1*) *Oxidative Degradation*

Ethyl cellulose has been shown to undergo considerable embrittlement upon exposure to oxygen at high temperature.[9,10] Axilrod and Kline[11] reported that, after three months of outdoor exposure, clear plastic sheets became opaque and brittle. Reports of this nature resulted in a large volume of empirical investigation directed toward finding antioxidants or inhibitors to prevent such deterioration.[12–17] The effectiveness of such

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[9] E. Berl and G. Rueff, *Cellulosechemie*, **14**, 44 (1933).

[10] H. Staudinger, H. Stock, and K. F. Daemisch, *Melliand Textilber.*, **22**, 620 (1941); *Chem. Abstracts*, **37**, 6889 (1943).

[11] B. M. Axilrod and G. M. Kline, *J. Research Natl. Bur. Standards*, **19**, 367 (1937).

[12] S. L. Bass, L. A. Rauner, and P. H. Lipke, Jr. (to The Dow Chemical Co.), U. S. Patent 2,383,361 (Aug. 21, 1943); *Chem. Abstracts*, **39**, 5487 (1945).

[13] G. M. Kline, Soc. of Plastics Ind. Conference, Los Angeles, Feb. 23, 1943.

[14] W. Koch (to Hercules Powder Co.), U. S. Patent 2,389,370 (Nov. 20, 1945); *Chem. Abstracts*, **40**, 1352 (1946); U. S. Patent 2,333,577 (Nov. 2, 1943); *Chem. Abstracts*, **38**, 2489 (1944).

[15] J. H. Sharphouse and J. Downing (to British Celanese Ltd.), Brit. Patent 578,286 (June 21, 1946); *Chem. Abstracts*, **41**, 3295 (1947); Brit. Patent 580,359 (Sept. 4, 1946); *Chem. Abstracts*, **41**, 3295 (1947).

materials in preventing breakdown of the plastic was measured in terms of the percentage of viscosity retention obtained under a given set of conditions of heat and availability of air or oxygen. This work was successful in permitting formulations to be described[17] which would reduce the sensitivity of the product to oxidative deterioration. During these investigations, several inconsistencies appeared which pointed to the need for a thorough knowledge of the basic mechanism involved in the oxidation.

The failure of the empirical method to provide a satisfactory answer to the problem can be attributed to three factors. First, viscosity retention was used as the criterion of stability. This is important from commercial aspects but since viscosity changes are a result of the degradation reaction, they are not a direct measure of the reaction causing the breakdown and cannot be relied upon to tell the complete story. Decomposition could occur, for example, so that cross-linkage would take place and the viscosity would either remain unchanged or in the extreme case could actually show an increase. This effect has actually been observed, and viscosity retentions of 118% or more are reported in the literature.[17] Second, an examination of the structure of the polymer, with its high concentration of ethoxyl linkages, would lead to the immediate assumption that oxidative degradation is analogous to the oxidation of simple ethers. From the abundant literature relative to oxidation of monomeric ethers[18–21] it can be concluded that the oxygen availability during exposure will greatly influence the ultimate viscosity achieved. Third, it is conceivable that the products of decomposition will also influence the rate of oxidation. The ultimate viscosity would then depend upon whether or not such materials could escape from contact with the cellulose derivative.

In order to establish the mechanism of the reaction, McBurney and Evans[22,23] measured the rate of oxygen absorption by ethyl cellulose under controlled conditions of temperature, pressure, and oxygen concentration. The initial experiments in this study showed the rate of oxygen absorption

[16] J. S. Tinsley (to Hercules Powder Co.), U. S. Patent 2,337,508 (Dec. 21, 1943); *Chem. Abstracts,* **38,** 3473 (1944); U. S. Patent 2,375,708 (May 8, 1945); *Chem. Abstracts,* **39,** 4521 (1945).

[17] B. Berry and W. Koch, *Modern Plastics,* **25,** 154 (Oct., 1947).

[18] A. M. Clover, *J. Am. Chem. Soc.,* **44,** 1107 (1922).

[19] N. A. Milas, *J. Am. Chem. Soc.,* **52,** 739 (1930); **53,** 221 (1931).

[20] C. Moureu and C. Dufraisse, *Chem. Revs.,* **3,** 113 (1926). *J. Soc. Chem. Ind.,* **47,** 819,848 (1928).

[21] H. Wieland and A. Wingler, *Ann.,* **431,** 317 (1923).

[22] L. F. McBurney, *Ind. Eng. Chem.,* **41,** 1251 (1949).

[23] E. F. Evans and L. F. McBurney, *Ind. Eng. Chem.,* **41,** 1256 (1949).

by ethyl cellulose to be a function of time as well as temperature. This observation was verified by oxidizing a series of samples under identical conditions; the samples, however, differed in both chain length and ethoxyl content. The induction periods for these samples were found to vary as did the initial rates of absorption. Once the steady state had been reached, the rates of oxygen absorption were quite similar in all cases as shown in Figure 80. The steady-state oxidation, therefore, is not a function of either the degree of substitution or the chain length of the polymer. Some explanation is required, however, for the variance observed in the induction periods of the different samples.

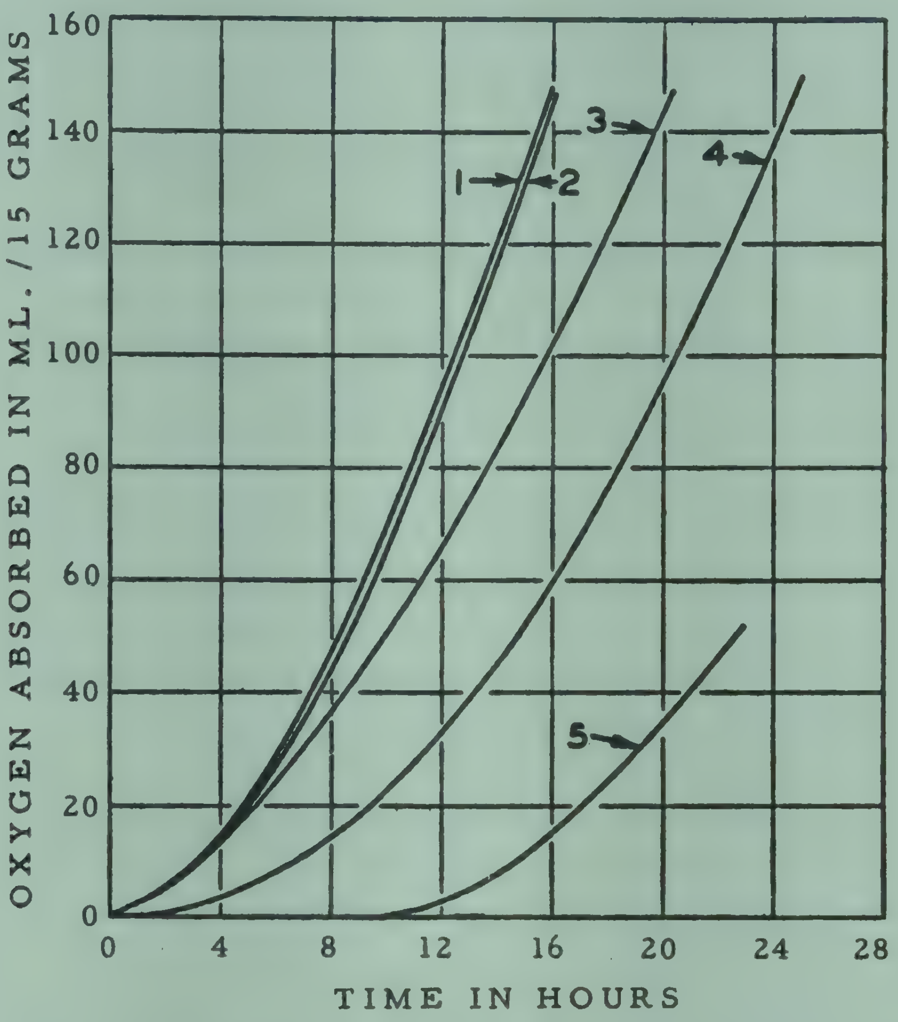


Fig. 80. Rate of oxygen absorption by various types of ethyl cellulose at 90 °C. (McBurney[22]). Samples were dried, ground films of ethyl cellulose. Ethoxyl content: curves 1 and 2, 48%; curve 3, 44%; curve 4, 44.5%; curve 5, 49.2%. Viscosity, 5% solution: curves 1 and 2, 1000 cps.; curve 3, 50 cps.; curve 4, 100 cps.; curve 5, 100 cps.

In reactions of this type an induction period may be an indication either of the presence of inhibitors, such as transition state metals, which are destroyed as the reaction proceeds, or of a truly autocatalytic process. With ethyl cellulose, it might be assumed that reaction would be initiated on an aldehyde group at chain ends. Such a process would follow a reaction course as illustrated below:

$$R_{ec}CHO + O_2 \longrightarrow [R_{ec}CO\cdot] + [\cdot HO_2] \quad (1)$$

$$[R_{ec}CO\cdot] + O_2 \longrightarrow [R_{ec}CO(OO\cdot)] \quad (2)$$

$$[R_{ec}CO(OO\cdot)] + R_{ec}H \longrightarrow R_{ec}CO(OOH) + [R_{ec}\cdot] \quad (3)$$

where R_{ec} stands for the ethyl cellulose residue exclusive of the atoms shown.

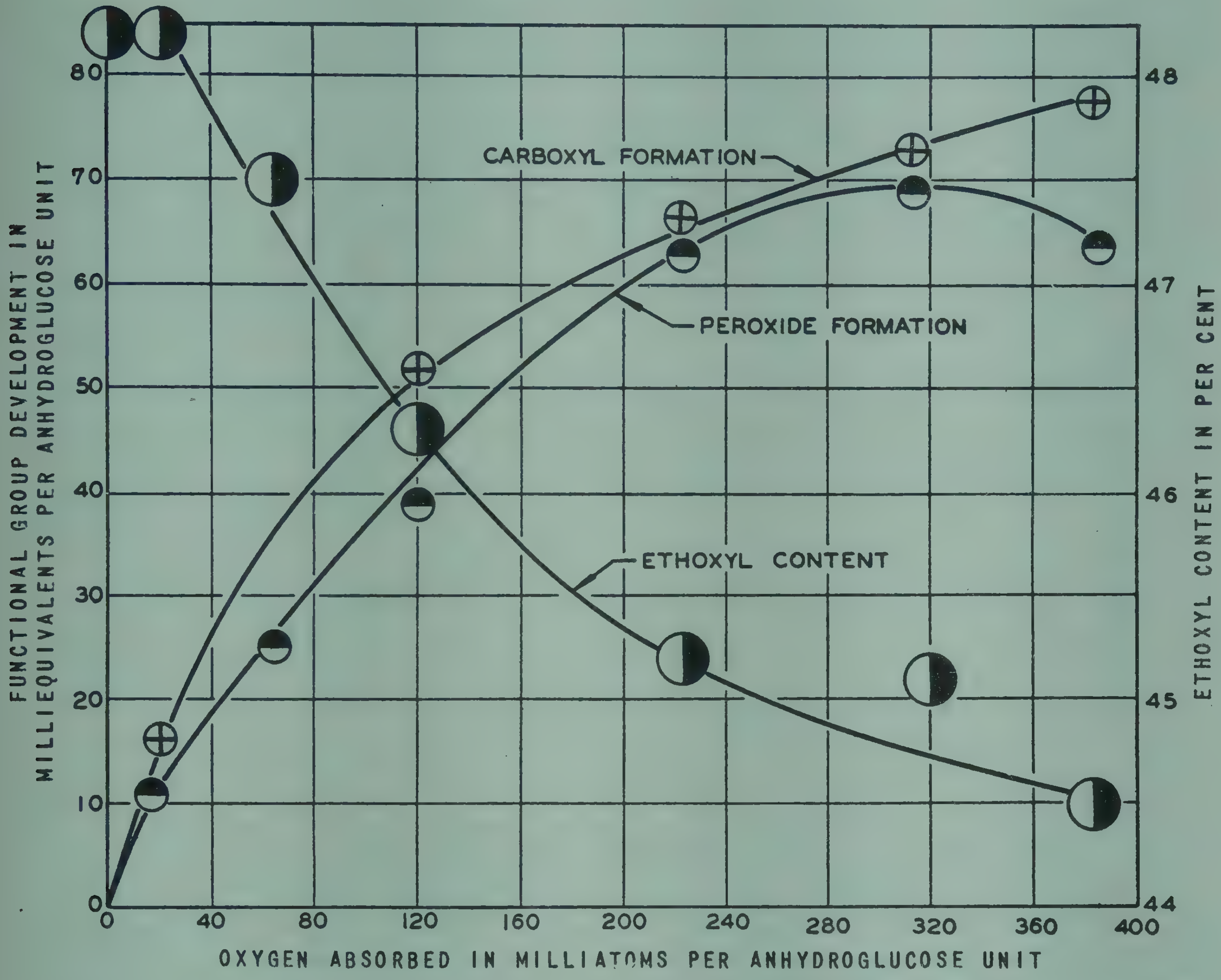


Fig. 81. Chemical changes accompanying oxygen oxidation of ethyl cellulose at 90 °C. (McBurney[22]). Dry, ground samples of ethyl cellulose were oxidized to various levels of oxygen absorption and the functional group content was measured.

If this interpretation is correct, the length of the induction period would be a function of the concentration of aldehyde groups as well as of the degree to which the oxidation may have progressed during storage or prior handling of the ethyl cellulose sample. It is reasonable to assume, consequently, that different samples will show varying induction periods. The correctness of this hypothesis was established for the ethyl cellulose oxidation by showing that the length of the induction period could be extended by removal of aldehyde end groups and shortened by the addition of free-radical sources. This evidence indicated that oxidation by molecular oxygen was autocatalytic and that it proceeded by means of a peroxide mechanism.

Further substantiation was obtained by measuring the hydroperoxide development during degradation as well as the formation of carboxyl groups and the effect of oxidation on the ethoxyl content. These data are illustrated in Figure 81 where it can be observed that peroxide content shows a rapid initial increase and reaches a maximal value. At higher degrees of absorption the measured values show a decrease in magnitude. Concurrently the carboxyls show an initial rapid increase which then becomes slower although giving no evidence of reaching a maximum value. The ethoxyl content, on the other hand, shows a short interval of no change followed by a rapid and then a diminishing rate of decrease.

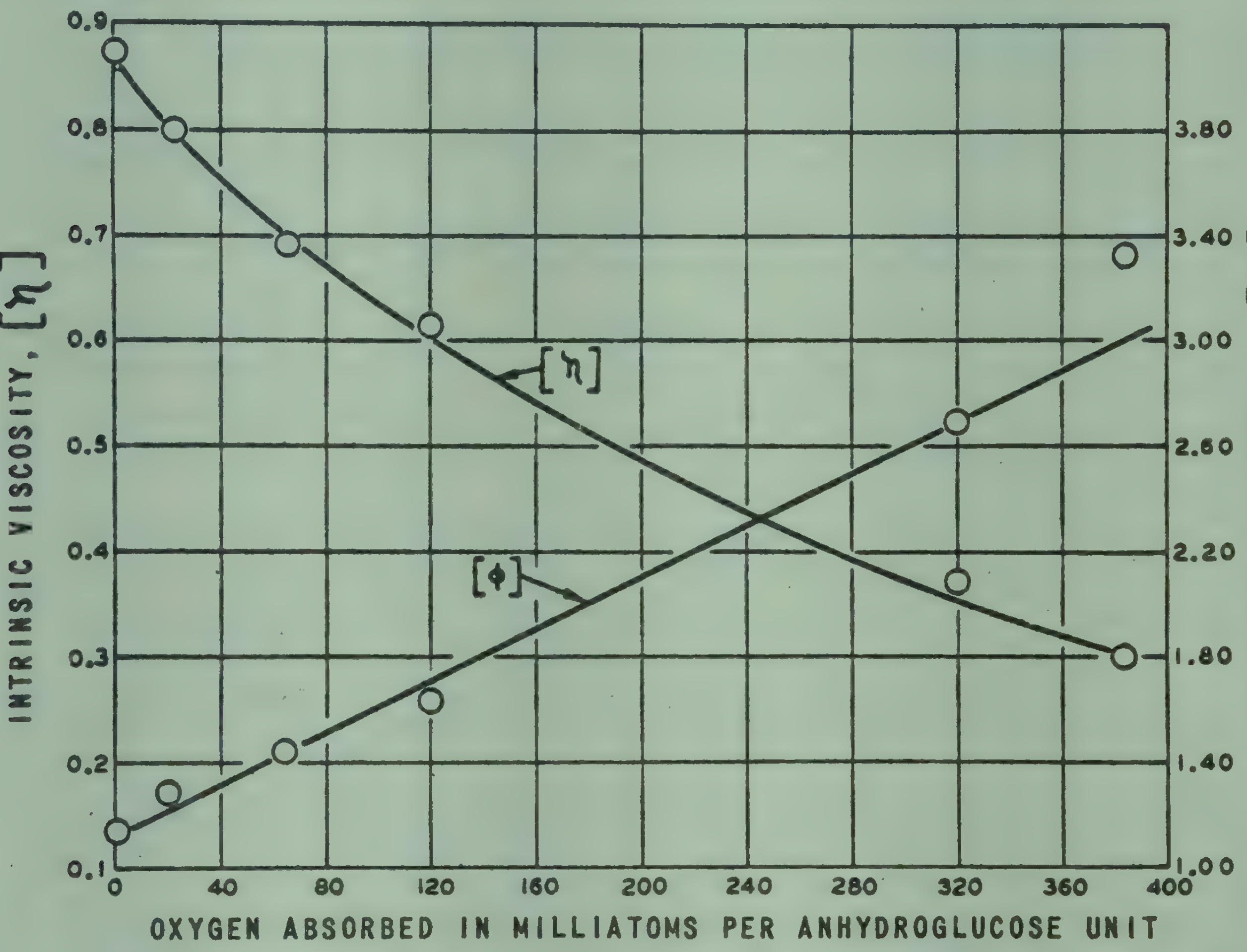


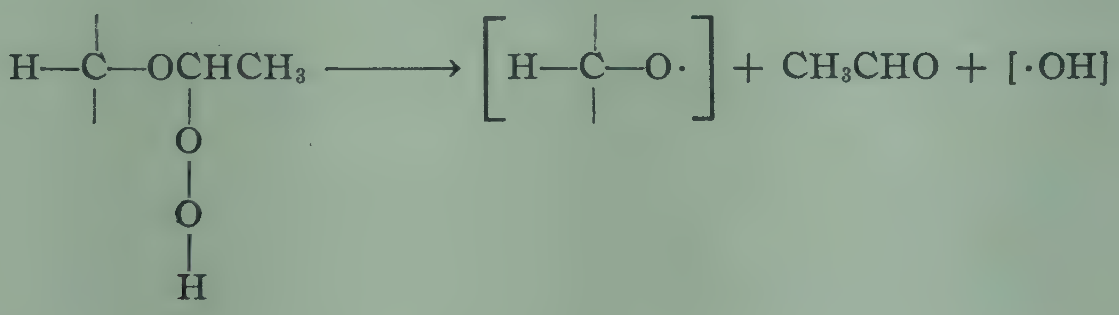
Fig. 82. Heat degradation of ethyl cellulose at 90 °C. as shown by changes in intrinsic viscosity and intrinsic fluidity (McBurney[22]). Samples were dried, ground films of ethyl cellulose.

These findings are of major importance in assigning an over-all mechanism to ethyl cellulose peroxidation. The character of the peroxide formation curve is indicative of the controlling step in the oxidation—that of peroxide formation by oxygen attack, followed by peroxide decomposition.

In all probability the peroxide decomposition is initially thermal in nature, since no salts, acids, or bases were present. As reaction progresses, it is conceivable that further breakdown is the resultant of thermal and acid catalysis, the latter arising from the carboxyls generated during the process. In simultaneous reactions of this type, a point is reached at which the rate of decomposition is so great that the measured peroxide content shows a decrease, although the rate of oxygen absorption by the sample has shown no change.

The initial rapid carboxyl development may be a reflection of the induction mechanism previously postulated, in which a peracid is formed from the aldehyde end groups present in the molecule. The propagation of the reaction does not require end groups alone, and for that reason the rate of carboxyl development shows a decrease and approaches a steady state with oxygen absorption.

This conclusion is further substantiated by the behavior of the ethoxyl content. The data show clearly that extensive oxidation is accompanied by a considerable loss in ethoxyl. It is justified, therefore, to assume that a major portion of the attack must be on the ethoxyl groups present in the molecule. This reaction can be pictured thus:



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}O\underset{\substack{|\\ O\\ |\\ O\\ |\\ H}}{C}HCH_3 \longrightarrow \left[H{-}\overset{|}{\underset{|}{C}}{-}O\cdot\right] + CH_3CHO + [\cdot OH]} \qquad (4)$$

The occurrence of this cleavage has been substantiated by isolating acetaldehyde in appreciable quantities from the oxidized ethyl cellulose. The nature of the ethoxyl loss curve also lends further support to the proposed mechanism in that during the initiation stage of the reaction the ethoxyl content does not change. Such a behavior would be required since the initial oxygen attack has been postulated to be on an end group and/or on an impurity not on the ethoxyl groups.

The structural inhomogeneities in cellulose derivatives make it of primary importance from mechanistic considerations to establish that the oxygen absorption rates are a true measure of the reaction kinetics and not simply a measure of rate of oxygen diffusion into the polymer. Measurement of the activation energy of the reaction in the temperature range of 69–90°C. gave a value of 25,000 cal. A value of this magnitude was considered to be sufficiently high to indicate that diffusion was not the controlling factor. The random nature of the oxidation received further support from the intrinsic viscosity and fluidity changes which occur during oxidation. These data are shown in Figure 82, as is also the linear relationship between the intrinsic fluidity and oxygen absorption in confirmation of the random nature of the oxidation (see Chapter III-C).

The discussion of the oxidative stability of ethyl cellulose thus far has been concerned with two major factors only: heat and air, or oxygen. The third important variable in outdoor weathering is the effect of light on the stability of cellulose ethers. Ultraviolet radiation has been found to be a catalyst for the molecular oxygen oxidation of ethyl cellulose.[23] The extent to which the rate of oxygen absorption is accelerated is shown in Figure 83. With illumination, the induction period is greatly reduced over the dark reaction, and the rate of reaction at the steady state is also markedly increased. This figure also serves to illustrate another important consideration, namely, the lack of a post-irradiation effect. The rapid decrease in oxygen absorption rate upon turning off the illuminating source is evidence that, in this system, no post-irradiation effect is present. The develop-

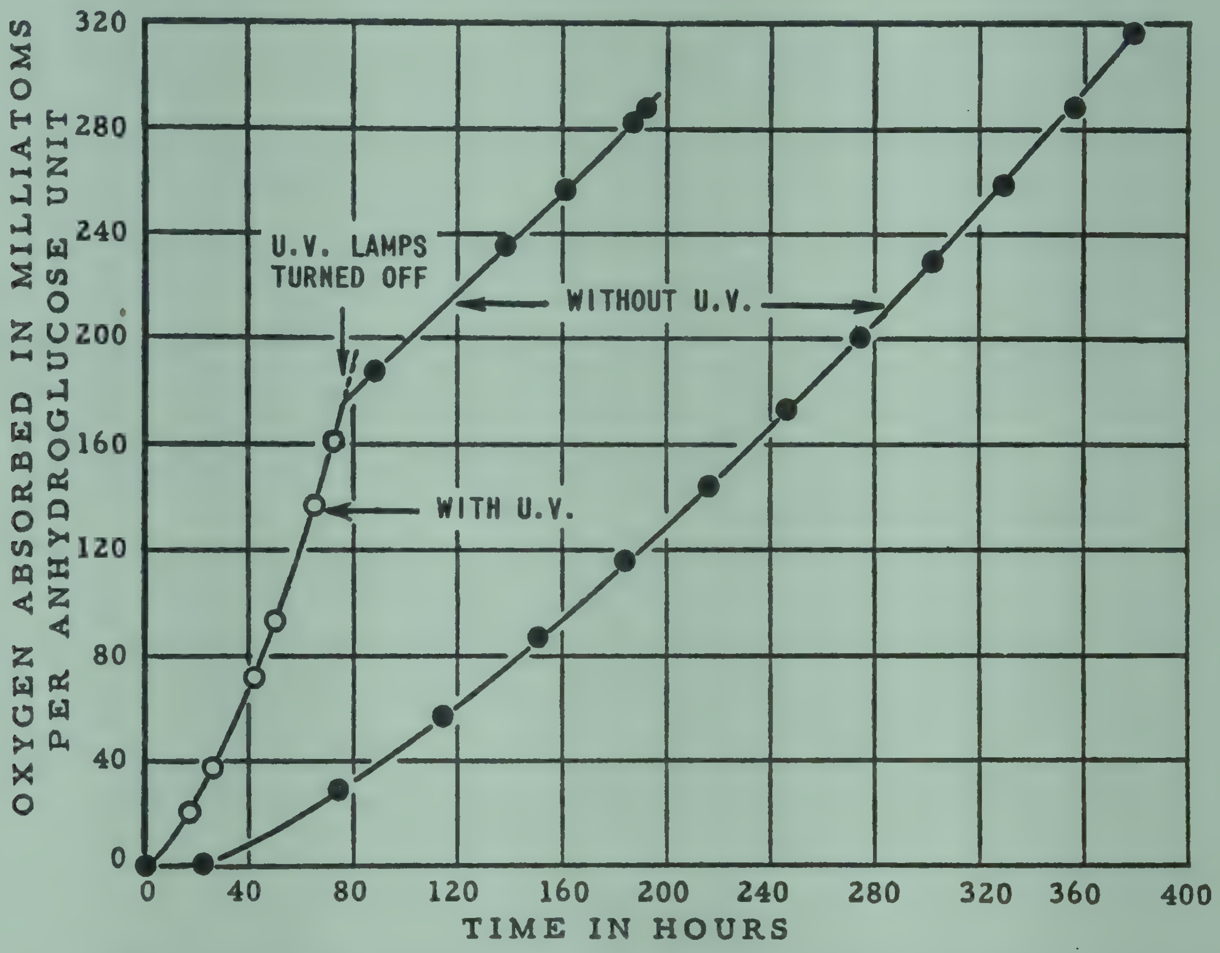


Fig. 83. Oxidation of ethyl cellulose at 50 °C. with and without ultraviolet (U.V.) light (Evans and McBurney[23]). Samples were dried, ground films of ethyl cellulose (48.2% ethoxyl content; viscosity of 5% solution in 8:2 toluene:2B alcohol, 14 cps.).

ment of peroxides and carboxyl groups and the loss of ethoxyl are quite similar with or without ultraviolet as was the change in viscosity and fluidity.

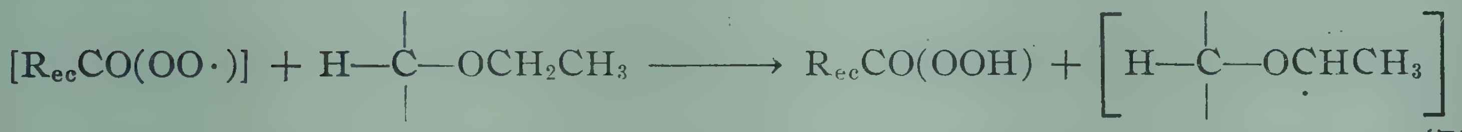
The general similarity of data for the samples oxidized with and without ultraviolet light indicates that there is no essential difference in the mechanism of oxidation. The only striking dissimilarity lies in the greatly accelerated rate of oxygen absorption in the presence of ultraviolet. This conclusion is similar to that expressed by Milas[19] for similar autoxidation of monomeric ethers. The ultraviolet behaves entirely as a catalyst as is to be expected if the reaction is chain propagative in character.

From the facts which have been discussed and also by analogy between this and similar reactions,[24] it is possible to deduce a reasonable mechanism for the oxidation of ethyl cellulose as follows:

Initiation

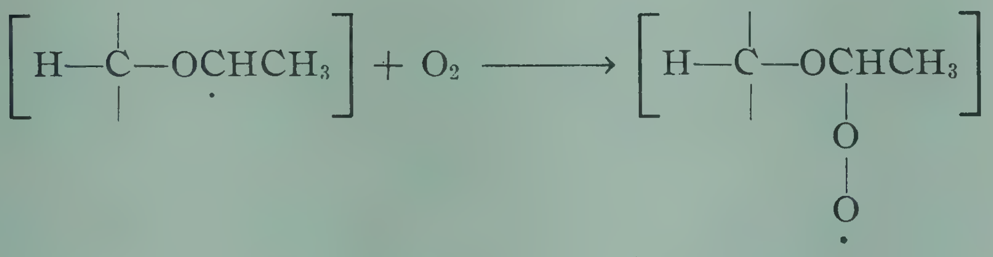
$$R_{ec}CHO + O_2 \longrightarrow [R_{ec}CO\cdot] + [\cdot OOH] \qquad (5)$$

$$[R_{ec}CO\cdot] + O_2 \longrightarrow [R_{ec}CO(OO\cdot)] \qquad (6)$$

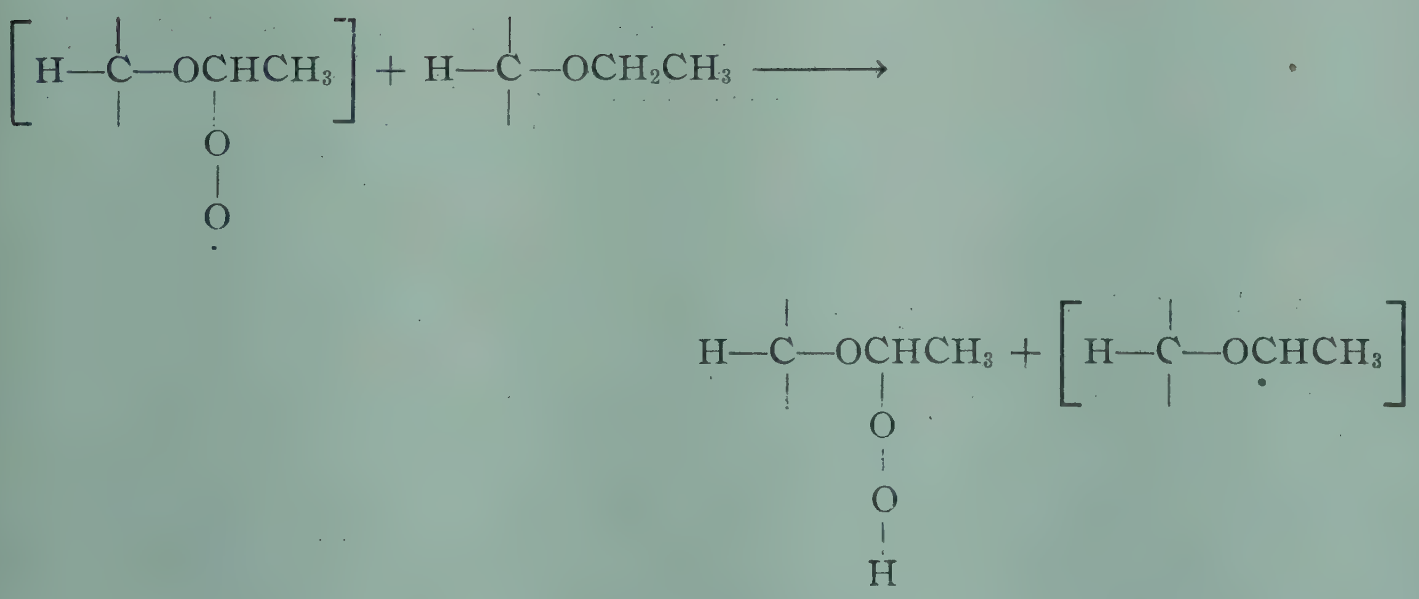


$$[R_{ec}CO(OO\cdot)] + H-\overset{|}{\underset{|}{C}}-OCH_2CH_3 \longrightarrow R_{ec}CO(OOH) + \left[H-\overset{|}{\underset{|}{C}}-O\underset{\cdot}{C}HCH_3\right] \qquad (7)$$

Propagation



$$\left[H-\overset{|}{\underset{|}{C}}-O\underset{\cdot}{C}HCH_3\right] + O_2 \longrightarrow \left[H-\overset{|}{\underset{|}{C}}-O\underset{\underset{\underset{\cdot}{O}}{|}}{\underset{O}{\underset{|}{C}}}HCH_3\right] \qquad (8)$$



$$\left[H-\overset{|}{\underset{|}{C}}-O\underset{\underset{\underset{\cdot}{O}}{|}}{\underset{O}{\underset{|}{C}}}HCH_3\right] + H-\overset{|}{\underset{|}{C}}-OCH_2CH_3 \longrightarrow H-\overset{|}{\underset{|}{C}}-O\underset{\underset{\underset{H}{\underset{|}{O}}}{|}}{\underset{O}{\underset{|}{C}}}HCH_3 + \left[H-\overset{|}{\underset{|}{C}}-O\underset{\cdot}{C}HCH_3\right] \qquad (9)$$

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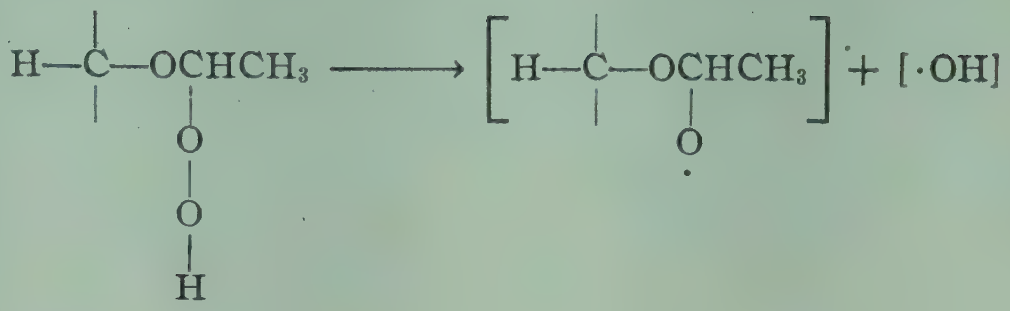
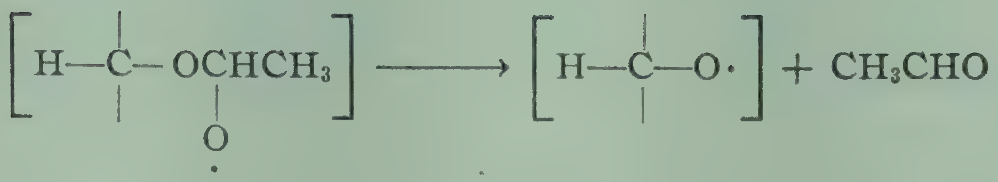
[24] W. A. Waters, *Ann. Repts. on Progress Chem.* (*Chem. Soc. London*), **42**, 130 (1945).

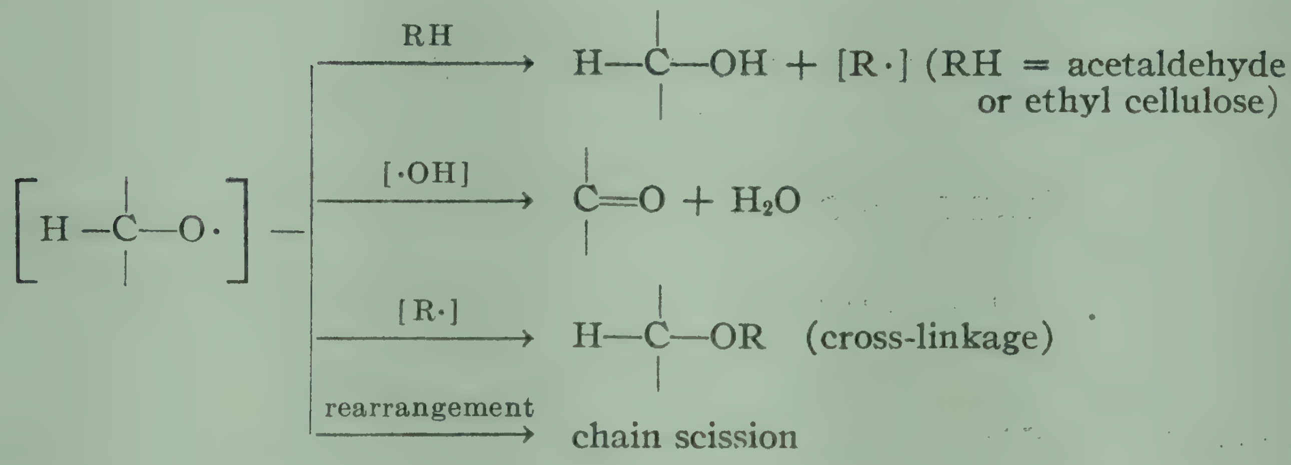
Decomposition



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}OCH(OOH)CH_3 \longrightarrow \left[H{-}\overset{|}{\underset{|}{C}}{-}OCH(O\cdot)CH_3\right] + [\cdot OH]} \tag{10}$$



$$\mathrm{\left[H{-}\overset{|}{\underset{|}{C}}{-}OCH(O\cdot)CH_3\right] \longrightarrow \left[H{-}\overset{|}{\underset{|}{C}}{-}O\cdot\right] + CH_3CHO} \tag{11}$$



$$\mathrm{\left[H{-}\overset{|}{\underset{|}{C}}{-}O\cdot\right] \xrightarrow{RH} H{-}\overset{|}{\underset{|}{C}}{-}OH + [R\cdot]} \text{ (RH = acetaldehyde or ethyl cellulose)} \tag{12}$$

$$\mathrm{\left[H{-}\overset{|}{\underset{|}{C}}{-}O\cdot\right] \xrightarrow{[\cdot OH]} \overset{|}{\underset{|}{C}}{=}O + H_2O} \tag{13}$$

$$\mathrm{\left[H{-}\overset{|}{\underset{|}{C}}{-}O\cdot\right] \xrightarrow{[R\cdot]} H{-}\overset{|}{\underset{|}{C}}{-}OR} \text{ (cross-linkage)} \tag{14}$$

$$\mathrm{\left[H{-}\overset{|}{\underset{|}{C}}{-}O\cdot\right]} \xrightarrow{\text{rearrangement}} \text{chain scission} \tag{15}$$

On the basis of this mechanism, the initiation of the reaction occurs on chain ends or aldehyde groups. Propagation of the oxidation does not require those end groups; rather it occurs on the ethoxyls along the chain. Chain termination is the resultant of the complex decomposition reaction of the celluloseoxy free radical. Reactions 12, 13, and 14 are hypothetical in that it is not possible to isolate materials corresponding to those indicated in the reaction scheme. Reaction 14, which would lead to the possibility of cross-linkage, has qualitative support in the reports of viscosity retentions in excess of 100% under certain conditions.[17]

The effectiveness of antioxidant can be seen by reference to Figure 84 in which the monobenzyl ether of hydroquinone has been employed as a retarder. The data in the graph show that the inhibitory effect is a function of concentration for the very low concentration and does not increase proportionally with increasing amounts.

In summary, then, it is possible to draw the following conclusions relative to the mechanism of ethyl cellulose oxidation:

1. Oxidation proceeds by means of a peroxide-catalyzed chain-propagated mechanism.
2. The reaction appears to be initiated on the end groups or aldehydes

present either initially in the chemical cellulose or developed during the ethylation reaction.

3. Chain propagation is accomplished by reaction on the ethoxyl groups, substituted along the polymer chain, to form hydroperoxides.

4. Formation of carboxyl groups, loss of ethoxyl, and polymer-chain scission are a result of the decomposition of ether hydroperoxides by thermal-catalyzed and/or acid-catalyzed mechanisms.

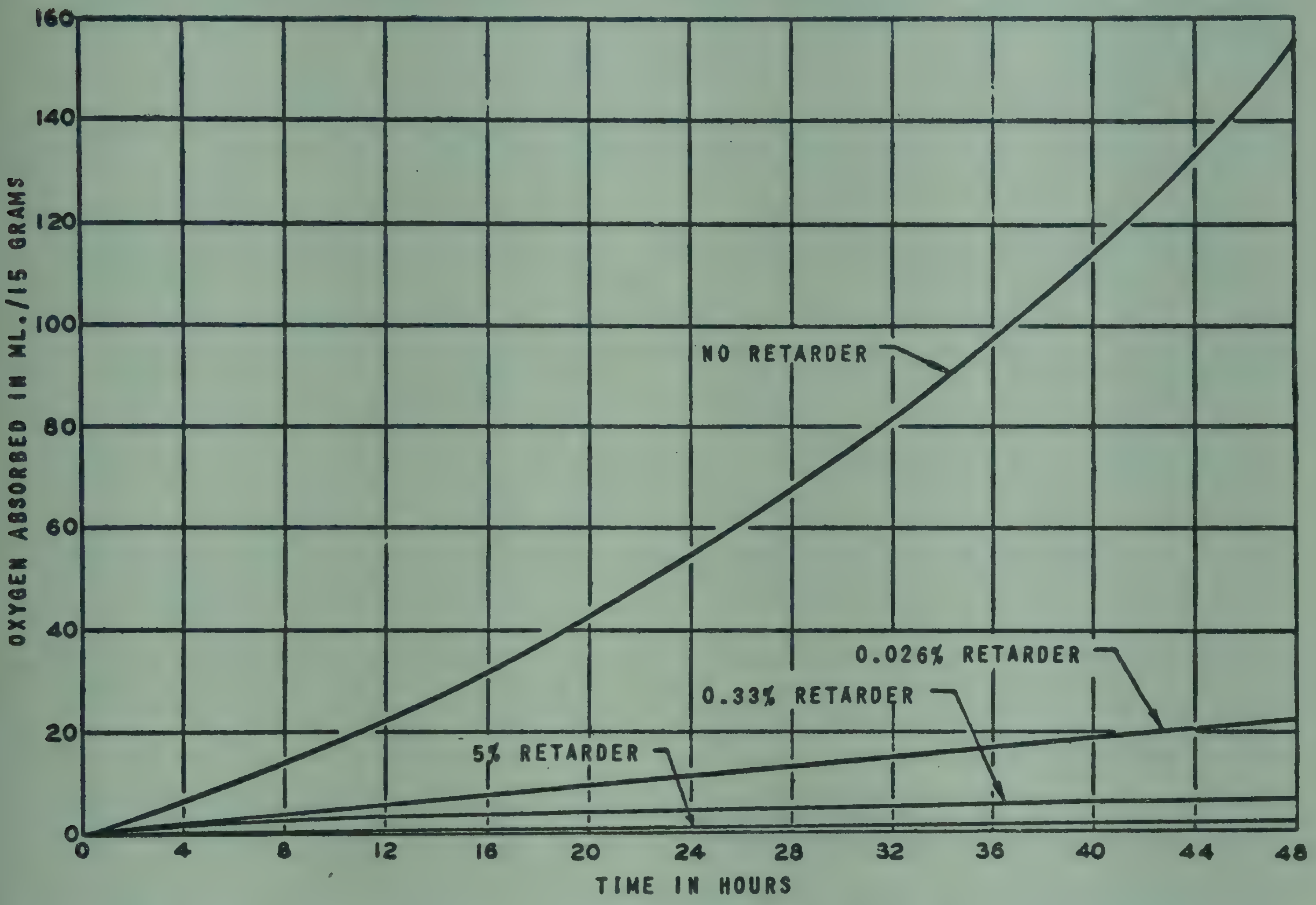


Fig. 84. Retardation of ethyl cellulose oxidation at 90°C. by hydroquinone monobenzyl ether (McBurney[22]). Retarder was incorporated in the ethyl cellulose samples prior to drying and grinding.

5. Oxidation is subject to positive catalysis by free-radical sources or ultraviolet light, and can be inhibited or retarded by typical free-radical chain terminators.

(b) CELLULOSE ORGANIC ESTERS

The organic esters of cellulose are the most stable of the cellulose derivatives under normal conditions of aging. Samples have been reported[25] to have retained their initial properties after storage for 25 years. At elevated temperatures, cellulose acetate, for example, may suffer degradation,[25–29] but it is many orders of magnitude more stable, under comparable conditions, than cellulose nitrate or cellulose ethers. Prolonged exposure of cellulose ester compositions to sunlight or to ultraviolet light brings about rather severe deterioration and produces a highly colored material with greatly reduced mechanical strength.[30–35] At relatively high temperatures, for example 160°C., cellulose acetate can be oxidized in a manner comparable to the cellulose ethers with a corresponding loss in desirable properties.[36]

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[25] L. Clément and C. Rivière, *Congr. chim. ind., Compt. rend. 18me Congr., Nancy,* **1938,** 703; *Chem. Abstracts,* **33,** 6042 (1939).

(*1*) *Oxidative Degradation*

Cellulose acetate, in contrast to materials such as alkali cellulose, ethyl cellulose, or benzyl cellulose, is quite resistant to oxidative decomposition, even at fairly high temperature; for example, ethyl cellulose will oxidize rapidly in an oxygen atmosphere at 90°C., whereas under similar conditions cellulose acetate is quite stable. If, however, the temperature is sufficiently high, for example 160°C., cellulose acetate will also oxidize as shown by a loss in strength, increase in color, and solubility changes.

The mechanism of the oxidation of this cellulose ester is rather obscure, in contrast to ethyl cellulose or similar ethers where the mode of oxygen attack can readily be understood. It is not possible to apply a similar mechanism to cellulose acetate oxidation. One of the major products of the acetate decomposition is carbon monoxide; hence, in order to follow the rate of oxygen absorption in closed systems, it is necessary to provide a means for the constant removal of this volatile decomposition product. It is also necessary that other materials such as water, carbon dioxide, and acetic acid be removed, because they too can influence the shape of the

[26] J. R. Hill and C. G. Weber, *J. Research Natl. Bur. Standards*, **17**, 871 (1936).

[27] P. Krais, *Leipzig. Monatschr. Textil-Ind.*, **43**, 257 (1928); *Chem. Abstracts*, **22**, 4828 (1928).

[28] C. J. Staud, *Paint, Oil and Chem. Rev.*, **89**, No. 18, 8 (1930).

[29] W. Wehr, *Kolloid-Z.*, **88**, 185 (1939).

[30] V. A. Karfunkel and D. A. Fedorov, *J. Applied Chem.* (*U. S. S. R.*), **13**, 1375 (1940); *Chem. Abstracts*, **35**, 2715 (1941).

[31] M. DeBuccor, *Papeterie*, **63**, 49 (1941).

[32] R. E. Montonna and C. C. Winding, *Ind. Eng. Chem.*, **35**, 782 (1943).

[33] S. Oguri, M. Takei, and N. Fujita, *J. Soc. Chem. Ind., Japan*, **42**, Suppl. binding, 54 (1939).

[34] T. S. Lawton, Jr., and H. K. Nason, *Ind. Eng. Chem.*, **36**, 1128 (1944).

[35] L. W A. Meyer and W. M. Gearhart, *Ind. Eng. Chem.*, **37**, 232 (1945).

[36] E. F. Evans and L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1260 (1949).

oxidation curves. When such precautions are taken, the curves of oxygen absorption versus time have the general characteristics shown in Figure 85. Curves 2, 3, and 4 were obtained under conditions of complete volatile by-product removal, whereas for curve 1 the carbon monoxide was not removed. This will serve to indicate the major effect such a volatile product will have on the apparent oxidation rate. In general, these curves are quite typical of an autocatalytic free-radical type of process. They show an induction period followed by a linear zero-order reaction which is characteristic of such processes.

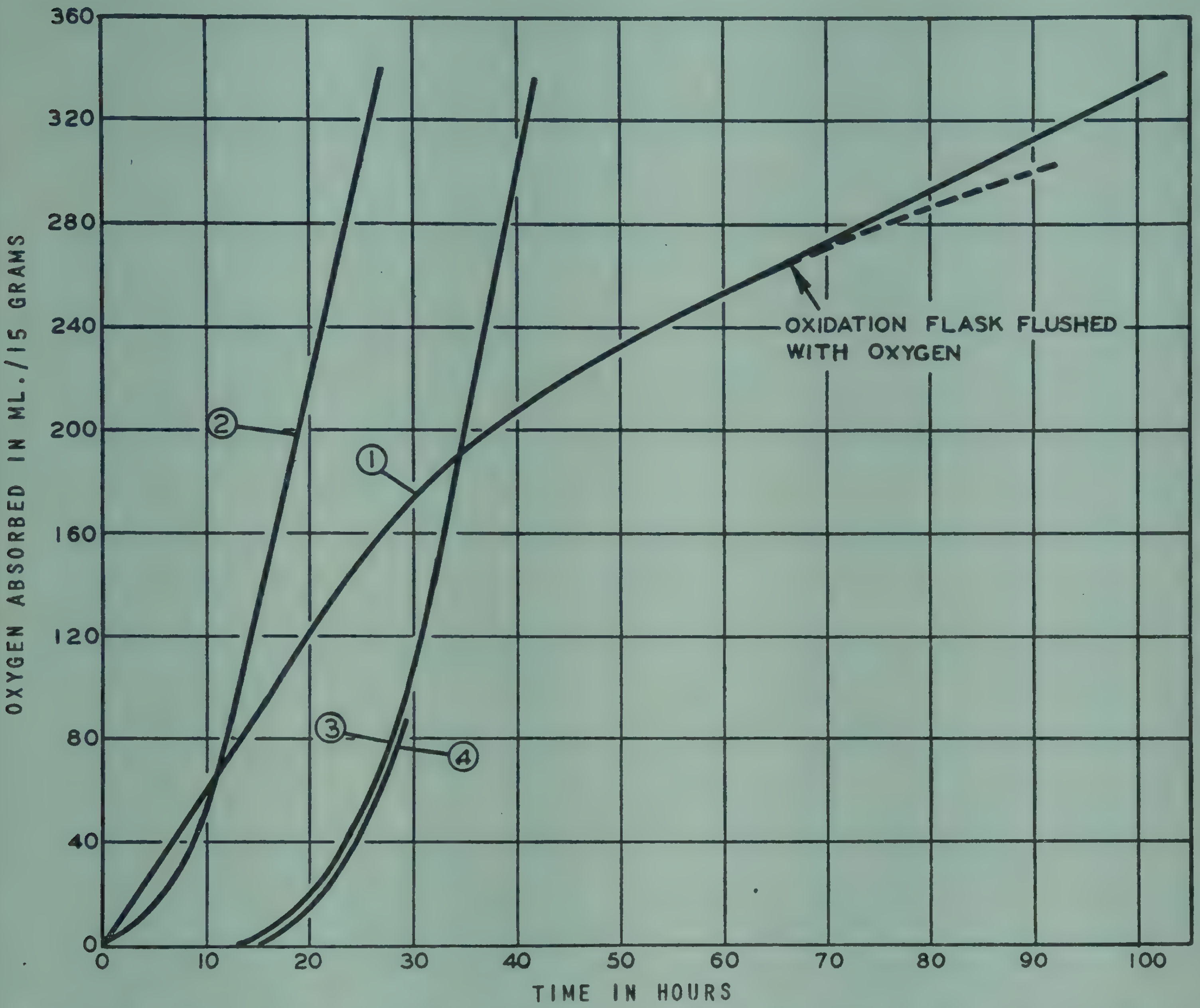

Fig. 85. Effect of carbon monoxide on oxidation of cellulose acetate at 160°C. (Evans and McBurney[36]). Curve 1: film-type granular cellulose acetate sample (55.5–56.5% combined acetic acid content), carbon monoxide not removed; Curve 2: same sample, carbon monoxide removed; Curves 3 and 4: plastics-type, granular cellulose acetate sample (52.5–53.5% combined acetic acid content), carbon monoxide removed.

The absorption of oxygen by cellulose acetate is accompanied by extensive chemical and physical changes in the molecule. In Figure 86 is illustrated the production of volatile products by this reaction. The upper curve is a composite of all volatiles produced (that is, water, carbon dioxide, and acetic acid) exclusive of the carbon monoxide. The development of the latter is shown by the lower curve. Whereas the production of volatiles other than carbon monoxide appears to be decreasing in rate with degree of oxidation, the carbon monoxide evolution gives evidence of being autocatalytic; it is constantly increasing with degree of oxidation.

The source of this carbon monoxide is not definitely known. Since α-ketocarboxylic acids[37] are known to give carbon monoxide upon pyrolysis, however, it is conceivable that such a structure is produced within the cellulose acetate molecule by oxidation, and the production of the carbon monoxide is then a secondary pyrolytic reaction of the oxidation.

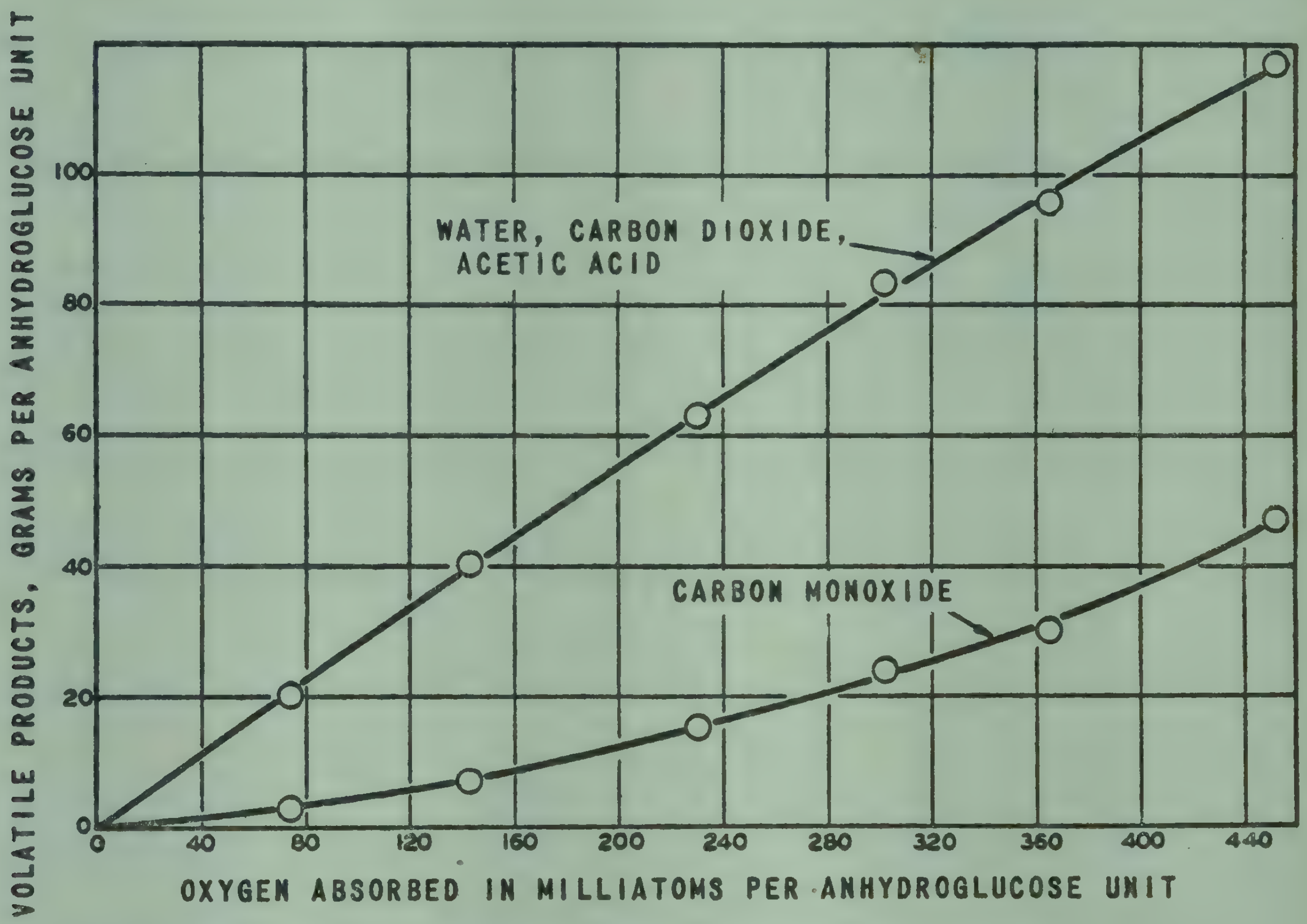

Fig. 86. Formation of volatile products during cellulose acetate oxidation at 160°C. (Evans and McBurney[36]). Sample was granular cellulose acetate with 60% combined acetic acid content.

From commercial aspects, freedom from color is an important factor in plastics applications. Oxidation of cellulose acetate has been found to be deleterious in this respect. From Figure 87 it can be seen that color formation during oxidation is a linear function of degree of oxidation over the entire range studied. Figure 87 also shows the changes in combined acetic acid content which occur for the same period of oxidation. These combined acetic results are somewhat in doubt. The values were obtained by two methods (see Chapter XII-B-2)—the saponification method and the method of Cramer, Gardner, and Purves[38]—and both methods gave similar results; that is, a trend toward higher combined acetic acid content as a result of oxidation. The need for this cross-checking was caused by the possibility of the formation of cellulosic carboxyls which would consume alkali in the saponification procedure and result in high values for combined acetic acid.

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[37] C. D. Hurd, *The Pyrolysis of Carbon Compounds*, Chemical Catalog Co., New York, 1929, pp. 556–9.

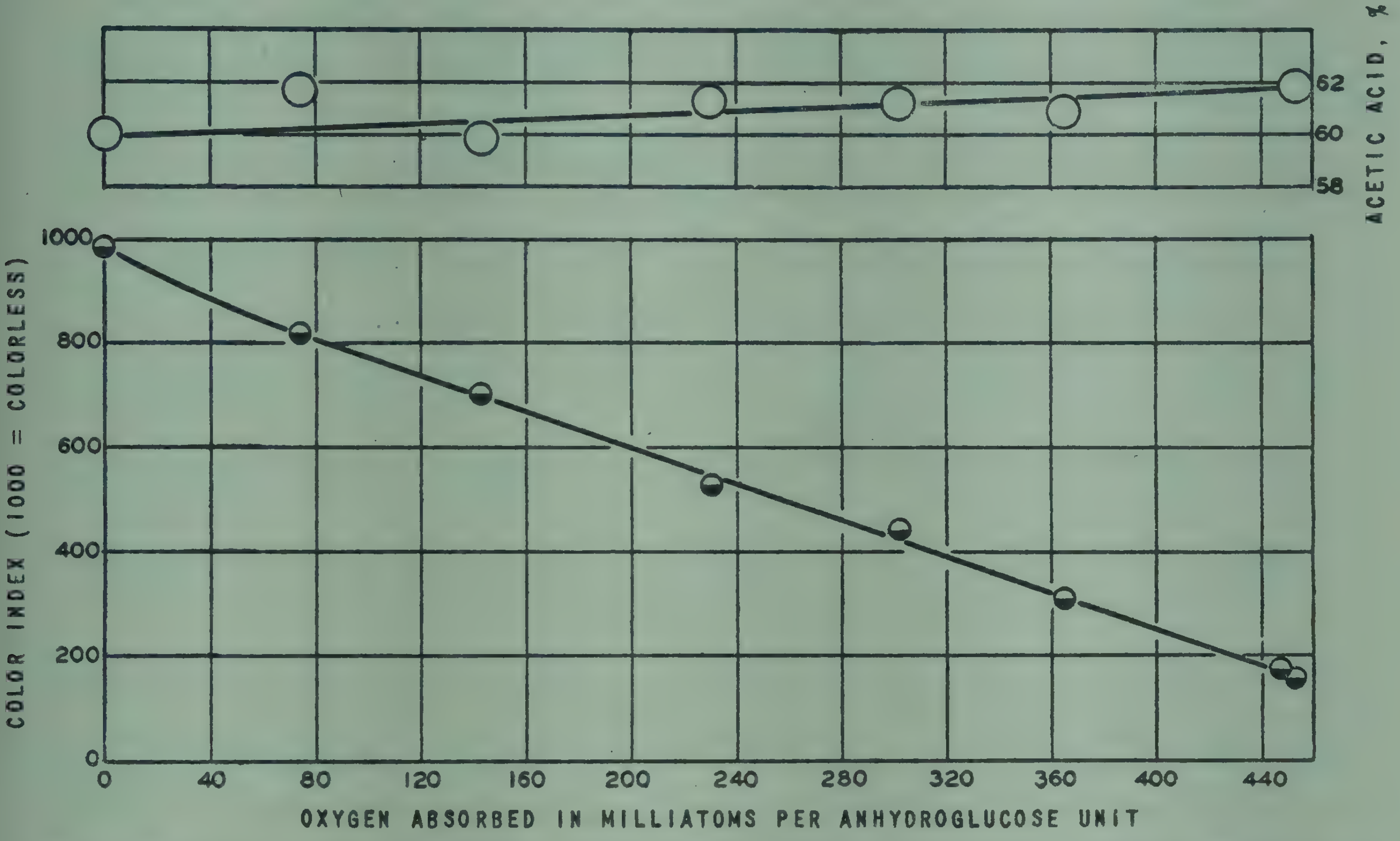

Fig. 87. Color and combined acetic acid content of cellulose acetate oxidized at 160°C. (Evans and McBurney[36]). Sample was granular cellulose acetate with 60% combined acetic acid content.

The viscosity of the cellulose acetate was lowered by oxidation as shown in Figure 88. In this plot the intrinsic viscosity and the change in intrinsic fluidity are shown. Here again from the commercial utility viewpoint, the change in viscosity is of primary importance; from the viewpoint of the mechanism of oxidation, however, the nature of the fluidity change curve is more revealing. In this case the change in intrinsic fluidity is linear up to an oxygen absorption of 240 milliatoms per anhydroglucose unit, after which the value begins to decrease. Since the intrinsic fluidity and chain breaks are related, it is apparent that the reaction has shifted from a normal random reaction to a more specific type of attack. The oxygen attack may, for example, have shifted to chain ends; consequently, the number of chain breaks for a given oxygen absorption would be greatly reduced. Since the mechanism of this oxidation is not known, such possibilities are purely speculation.

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[38] F. B. Cramer, T. S. Gardner, and C. B. Purves, *Ind. Eng. Chem., Anal. Ed.*, **15**, 319 (1943).

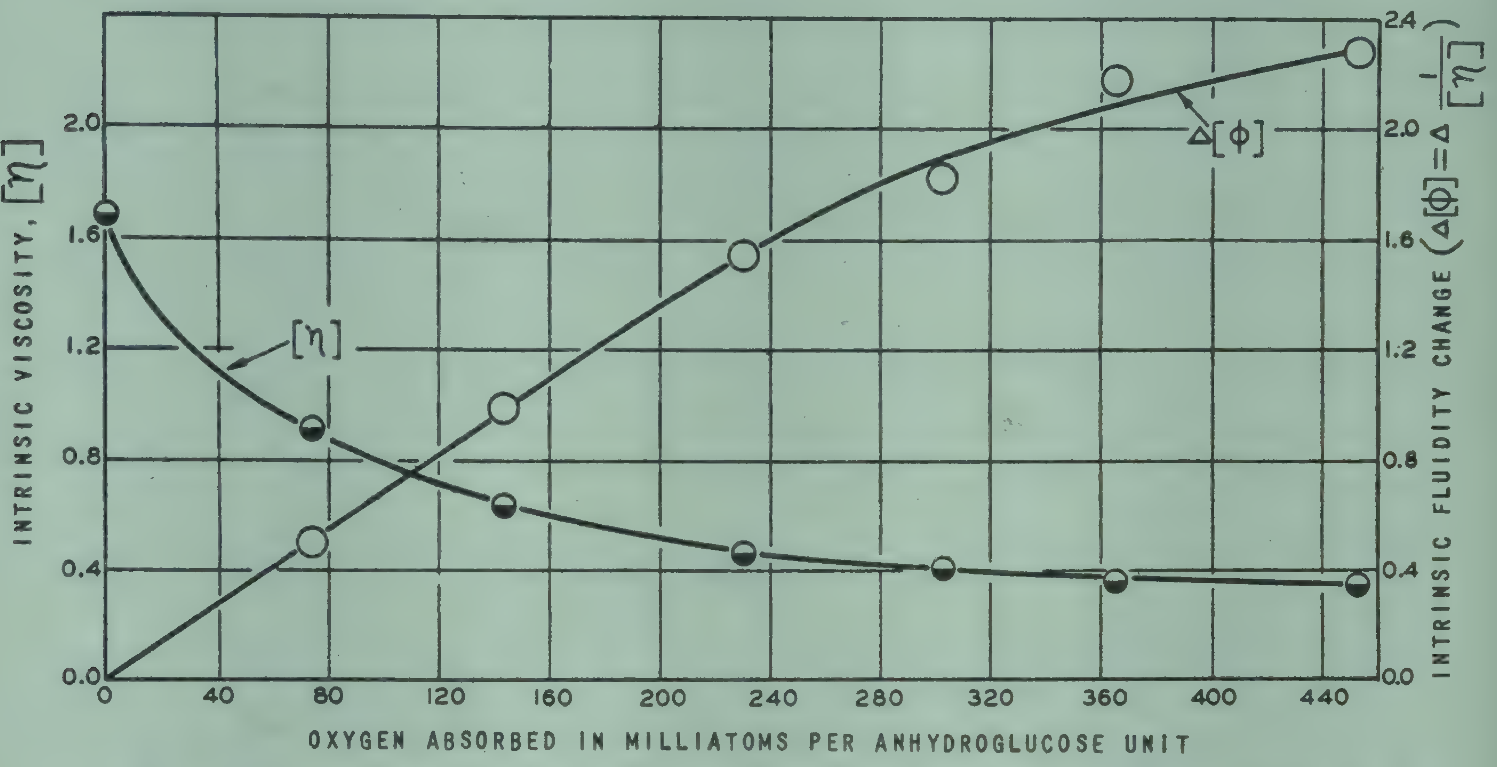

Fig. 88. Degradation of cellulose acetate on oxidation at 160°C. (Evans and McBurney[36]). Sample was granular cellulose acetate with 60% combined acetic acid content. The intrinsic fluidity change, Δ[ϕ], is the difference between the reciprocal of the intrinsic viscosity of the oxidized sample and that of the original cellulose acetate.

The autoxidation of cellulose acetate can be catalyzed by the presence of small amounts of acidic materials such as sulfuric acid. This is illustrated in Figure 89. Curves 5 and 6, for example, show the effect of the addition of 0.001% and 0.01% of sulfuric acid to the cellulose acetate sample whose basic oxidation rate is illustrated by curve 3. It is to be noted that these curves show a considerably different initial behavior from those in Figure 85; an immediate absorption of oxygen is followed by a period of relative inhibition, after which the typical free-radical absorption becomes dominant. In the case illustrated in Figure 89, the acetate had been cast as a film in order to permit the uniform introduction of trace amounts of catalysts. Even though these films were dried rigorously, it is apparent that some solvent has been tenaciously retained and has changed the initial absorption rates. This can be appreciated by a comparison of curves 1 and 3 in Figure 89. Curve 1 is a cellulose acetate flake as obtained from a plant batch, and curve 3 is the same material dissolved in acetone, cast as a film, dried and ground, then oxidized.

The data discussed thus far have emphasized the role of oxygen in the thermal degradation of cellulose esters. It is not to be implied, however, that oxygen is the sole contributor to the thermal instability of these polymers. The presence of another nonoxidizing mechanism is apparent from the data in Table 44 from the work of DeCroes and Tamblyn.[39] In this

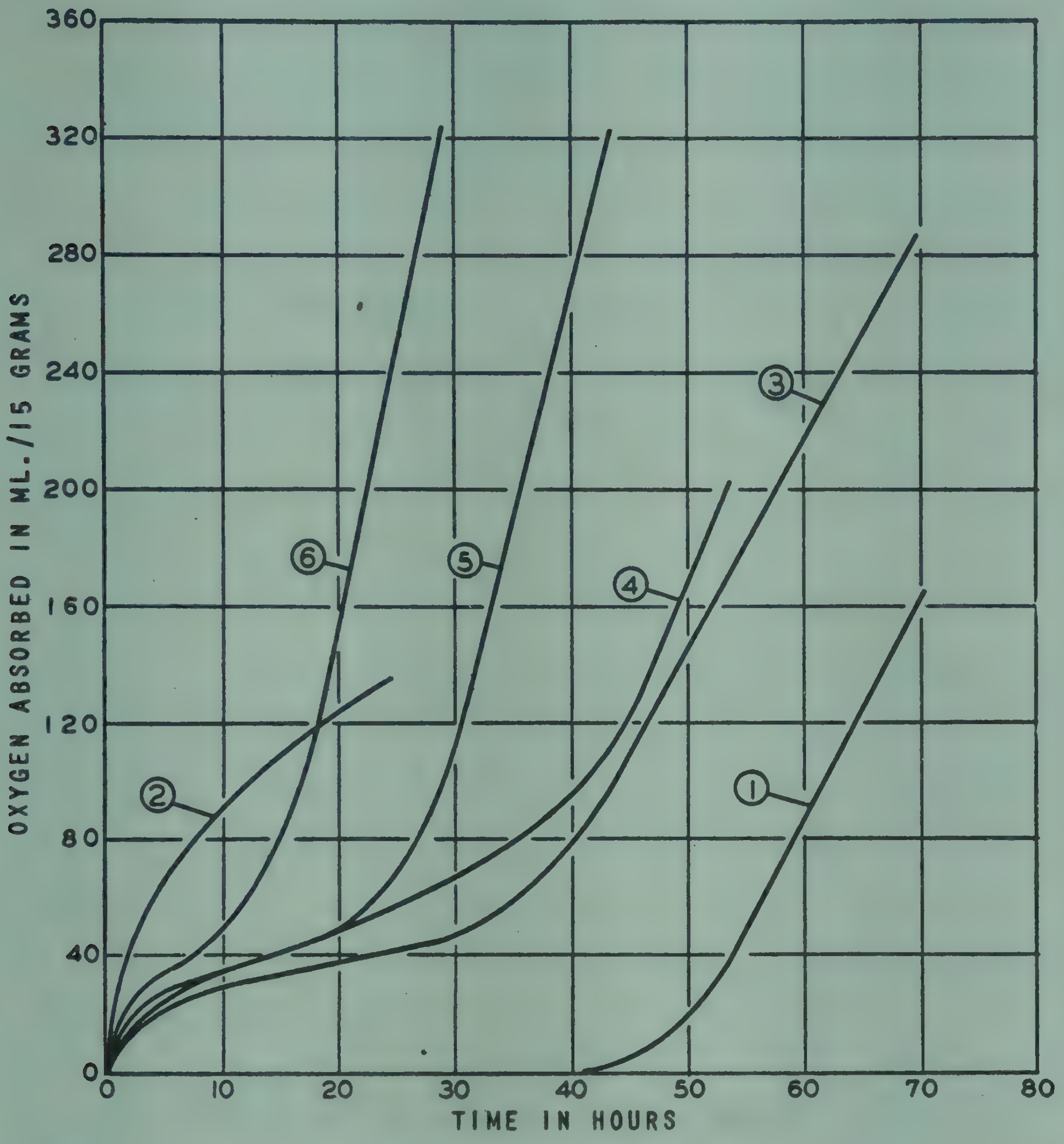

Fig. 89. Effect of acids and retained solvents on oxidation of cellulose acetate films at 160°C. (Evans and McBurney[36]). Curve 1: flake or granular commercial plastics-grade cellulose acetate with 52.1% combined acetic acid content; Curve 2: same sample as curve 1, but dissolved in acetone, dried in vacuum oven at 105°C. for 24 hr., ground, and then oxidized; Curve 3: same as curve 2, but dried in vacuum desiccator at room temperature; Curve 4: same as curve 3, but with 0.1% of a previously oxidized sample added; Curves 5 and 6: 0.001 and 0.01%, respectively, of H_2SO_4, based on cellulose acetate, added to cellulose acetate film.

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[39] G. C. DeCroes and J. W. Tamblyn, *Modern Plastics,* 29, 127 (April, 1952).

instance the cellulose acetate butyrate was used as an unplasticized powder to avoid any complications due to solvent or plasticizer interaction. The values in Table 44 indicate that in the absence of oxygen this ester will decompose thermally to a very considerable degree; in an atmosphere of oxygen, however, the degradation will be greatly increased.

TABLE 44

Oxidative and Thermal Degradation of Cellulose Acetate Butyrate (DeCroes and Tamblyn[39])

Conditions of exposure	Atmosphere	Apparent acetyl content, %	Color	Degradation in molecular weight, %
Unexposed	—	34.7	White	0
Exposed 24 hrs. at 150°C.	N_2	36.6	Brown	64
	O_2	37.2	Brown	81
Exposed 24 hrs. at 180°C.	N_2	37.2	Black	48
	O_2	37.2	Black	90

In actual practice, cellulose esters are always used in combination with plasticizers, which may exert a marked influence on the stability of the resulting plastic. Some of the more commonly used materials show a remarkable instability to oxygen and thus may actually behave as catalysts for the oxidation of the polymer. The oxidizability of some of these compounds is shown in Table 45. It is interesting to note that those plasticizers, such as dimethyl phthalate and triphenyl phosphate, which are inert to oxygen do not contain in their molecules either methylene or methylidene groups, which are known to be readily susceptible to oxidative

TABLE 45

Oxidizability of Plasticizers (DeCroes and Tamblyn[39])

Conditions: 25 ml. (or 25 g.) of plasticizer shaken under oxygen for 3 hr. at 150°C.

Plasticizer	Apparent oxygen absorbed, ml.	Acid produced, milliequiv.	Peroxide produced, milliequiv.
Dimethyl phthalate	0	0	0
Diethyl phthalate	26	2.0	1.3
Dibutyl phthalate	52	2.3	0.5
Bis(2-ethylhexyl) phthalate	42	1.5	0.7
Dibutyl sebacate	67	1.7	1.6
Tripropionin	20	1.8	1.0
Triphenyl phosphate	0	0	0

attack.[40,41] The ability of sensitive plasticizers to induce oxidation in cellulose acetate butyrate is illustrated in Table 46. These illustrations will suffice to show how the inherent oxidative sensitivity of organosoluble cellulose derivatives can be compounded and magnified by the plasticizer system with which they are formulated.

TABLE 46

Induced Oxidative Degradation of
Cellulose Acetate Butyrate (DeCroes and Tamblyn[39])

Conditions: 1 g. of ester in 25 ml. (or 25 g.) of plasticizer heated under oxygen for 3 hrs. at 150°C.

Plasticizer	Apparent oxygen absorbed, ml.	Degradation in molecular weight, %
None	0	0
Dimethyl phthalate	0	11
Triphenyl phosphate	0	1.5
Diethyl phthalate	29	86
Dibutyl phthalate	32	69
Bis(2-ethylhexyl) phthalate	84	76
Dibutyl sebacate	66	71
Tripropionin	39	80

Stability can be complicated even more by the presence of substances which will act as catalysts for the reaction. Included among these compounds are a number of heavy metal soaps such as cupric, ferric, nickelous, chromic, and silver stearate as well as pigments such as titanium dioxide.

The deleterious effects of plasticizers and catalysts fortunately can be greatly reduced by the use of antioxidants or inhibitors such as 2,6-di-*tert*-butyl-*p*-cresol, *N*-*tert*-butylaniline, *N*-phenylglycine, and 2-[*N*-ethyl-*N*-(*p*-nitro-*p*-phenylazoanilino)]ethanol. The importance of proper choice of stabilizer and plasticizer systems in compounding cellulose ester plastics cannot be overemphasized.

Ultraviolet light plays as important a role in the degradation of cellulose esters exposed to outdoor weathering as it does with the cellulose ethers. Some breakdown is experienced by the esters in an inert atmosphere, but it is quite minor in comparison to the effect obtained with air or oxygen present. The magnification of the ultraviolet instability of cellulose acetate butyrate by the oxygen in air can be seen from the data in Table 47. Plasticizers will have an effect in the ultraviolet-catalyzed oxidation similar to

[40] R. Criegee, H. Pilz, and H. Flygare, *Ber.*, **72B**, 1799 (1939).

[41] P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

that shown in the heat-catalyzed reaction. With ultraviolet, a further complication is introduced in that there are considerable variations in the ultraviolet absorptive capacity of the various plasticizers used in formulation. Meyer and Gearhart[35] have reported that aromatic plasticizers even contribute some protection against breakdown by virtue of their increased absorption over that of the aliphatic plasticizers. Organic inhibitors such as phenyl salicylate are remarkably effective in stabilizing cellulose esters toward ultraviolet-induced oxidation.

TABLE 47

Breakdown of Cellulose Acetate Butyrate in Sealed Quartz Tubes Exposed to Ultraviolet Light

(DeCroes and Tamblyn[39])

Exposure, 800 hrs. in Weather-Ometer	Degradation in molecular weight, %
Unprotected	44
Sealed in air	44
Sealed in nitrogen	12

Egerton[42] has investigated the photochemical degradation of cellulose acetate rayon yarns dyed with dispersed and soluble acetate dyes. The effect of such substances on the stability of the yarn is quite minor, in contrast to the corresponding instability observed with dyed cotton (see Fig. 33, Chapter III-C-4). In several cases the loss in strength of the dyed yarn is less than that of the undyed acetate rayon exposed under identical conditions. The extent to which the degradation does occur is largely dependent upon the relative humidity of the surrounding atmosphere; in most cases loss in strength is negligible at 0% relative humidity. The maximum deterioration is usually observed at a relative humidity of 100% as shown in Table 48.

There does not appear to be any good correlation between the color shade and its sensitizing action on the acetate rayon, a behavior which is distinctly different from that observed with dyed cotton (see Fig. 33, Chapter III-C-4). These data can be interpreted to indicate that the breakdown is the result of an oxidation process in which hydrogen peroxide is formed and then actually causes the oxidative degradation. The relative inertness of cellulose acetate toward hydrogen peroxide explains the minor effects observed on its tensile strength, and the effect of high humidity is understandable on the basis of its being required for the production of hydrogen peroxide.

[42] G. S. Egerton, *Am. Dyestuff Reptr.*, **38**, 608 (1949).

The outdoor weathering stability of cellulose acetate can be summarized as follows:

1. Cellulose acetate will undergo a heat-catalyzed and light-catalyzed oxidation which will result in an increase in color, a loss in tensile strength, and the production of volatile by-products such as CO, CO_2, water, and acetic acid.

TABLE 48

Loss in Tensile Strength of
Solacel-Dyed Cellulose Acetate Yarns (Egerton[42])
Conditions: Exposed to sunlight for 4 months (June–Sept.)

Solacel Dye	Loss in tensile strength, % 0% relative humidity	 100% relative humidity
None	14	21
Fast Yellow G	0	1
Fast Orange 2GK	0	3
Fast Scarlet B	1	3
Fast Crimson B	0	5
Fast Red 5BG	2	3
Violet B	7	10
Violet R	0	5
Fast Green 2G	0	5
Fast Blue 2B	6	4
Navy Blue G	0	7

2. Cellulose acetate will also undergo a strictly thermal decomposition with deleterious effects comparable to those above.

3. Plasticizers, heavy metal soaps, pigments such as titanium dioxide, and acids such as bound sulfuric acid may act as positive catalysts for the reaction.

4. The oxidative breakdown can be inhibited by the proper choice of antioxidants and plasticizer systems.

5. The exact mechanism of the reaction is not known with any degree of certainty.

(c) CELLULOSE INORGANIC ESTERS

Cellulose nitrate (also called nitrocellulose) is the only inorganic cellulose ester of commercial importance. It is unique among the industrially significant high polymers because of its ability to decompose exothermically without the participation of oxygen. In spite of this, it is satisfactorily stable under ordinary conditions if high temperatures are avoided, alkaline or even slightly basic materials are not used in its formulation, and there is reasonable protection from ultraviolet light.

Solutions of cellulose nitrate are known to undergo an aging reaction which results in a lowered viscosity (see Section B of this Chapter IX). Both Wehr[43] and Campbell and Johnson[44] have reviewed the literature relative to this phenomenon and have drawn the following general conclusions:

"(1) Cellulose nitrate solutions, on standing in the dark, show a decrease in viscosity. (2) The decrease in viscosity is accelerated by standing in strong light. (3) The decrease in relative viscosity is more marked the more concentrated the solution. (4) The decrease in viscosity is more marked in the early than in the late stages of the aging process. (5) The decrease in viscosity has been observed with solutions in acetone and in many other solvents."

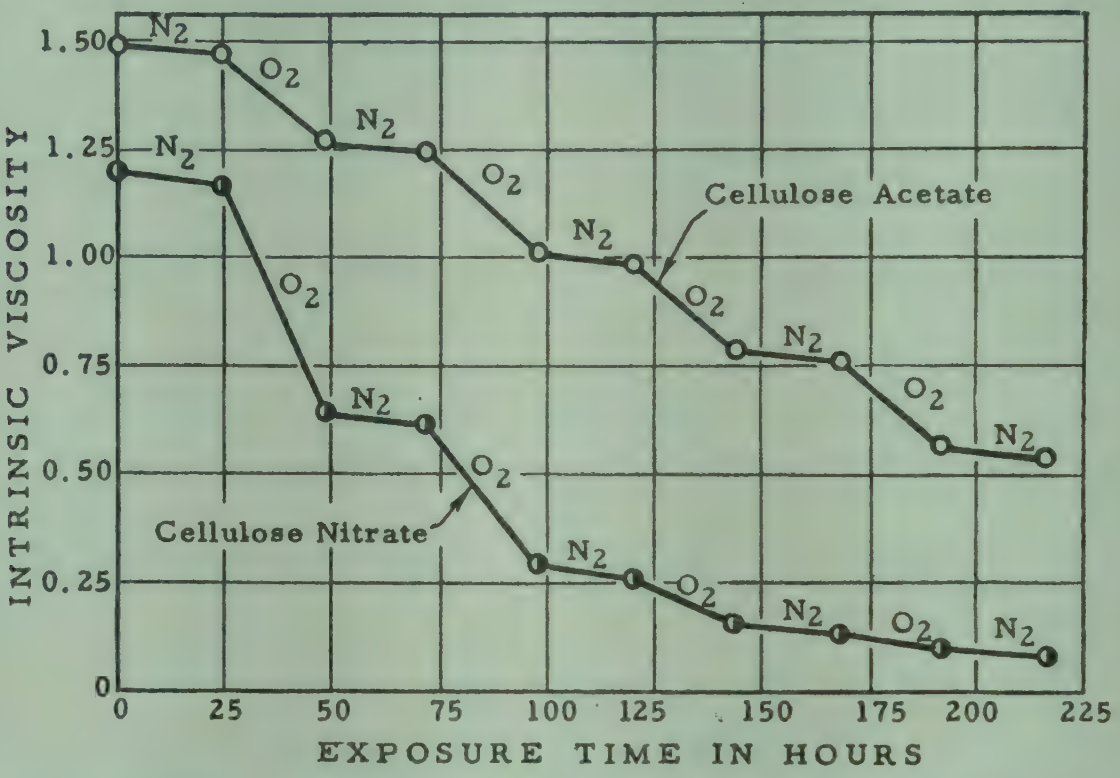

Fig. 90. Degradation of cellulose acetate and cellulose nitrate in the presence of ultraviolet light at 60°C. (Lawton and Nason[34]). Samples of cellulose acetate (38.0% acetyl content) and cellulose nitrate (11.10% N) cast as 0.005-in. films were exposed to ultraviolet light in alternate atmospheres of nitrogen and oxygen.

(1) Oxidative Degradation

The breakdown of cellulose nitrate in film form under ultraviolet irradiation is greatly accelerated by the presence of oxygen. This can best be illustrated by examining the data in Figure 90 taken from the work of Lawton and Nason.[34] In this example, cellulose acetate and cellulose nitrate films are compared under the same conditions. The greatly increased rate of viscosity change in the atmosphere of oxygen is readily apparent.

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[43] W. Wehr, *Kolloid-Z.*, 88, 185, 290 (1939).

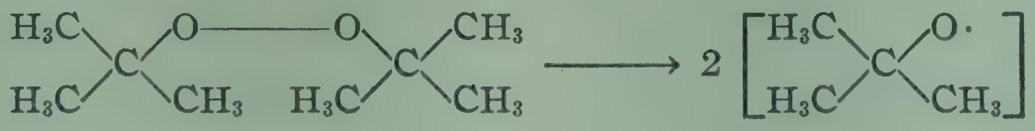
[44] H. Campbell and P. Johnson, *J. Polymer Sci.*, 5, 443 (1950).

Inorganic peroxides also have a catalytic effect on cellulose nitrate degradation similar to that of oxygen. The common oxidation and polymerization inhibitors of the neutral type, such as hydroquinone, are effective in retarding the rate of decomposition.

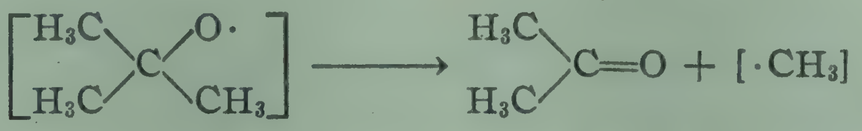
The action of oxygen in these ultraviolet-catalyzed degradations may be secondary. The denitration reaction produces NO_2 and HNO_3 as well as organic reducing materials. The latter convert the NO_2 to NO. In all probability, the oxygen acts merely as a reagent for the reconversion of NO to NO_2 and HNO_3. The latter compounds will cause further degradation of the cellulose nitrate and liberation of nitrogen oxides, instigating an autocatalytic process. It is more likely, therefore, that oxygen cannot be considered as a primary factor in cellulose nitrate deterioration, but merely as a secondary contributor to the over-all mechanisms.

(2) *Thermal Degradation*

The chief source of degradation of cellulose nitrate is its extreme thermal sensitivity. Nitric esters are very similar to organic peroxides in the chemistry of their decomposition. In both cases, there is a weak link which can be broken with an activation energy of approximately 40,000 cal. This analogy is illustrated by comparing the decomposition of *tert*-butyl peroxide (equations 17 and 18) and cellulose nitrate (equations 19–21).

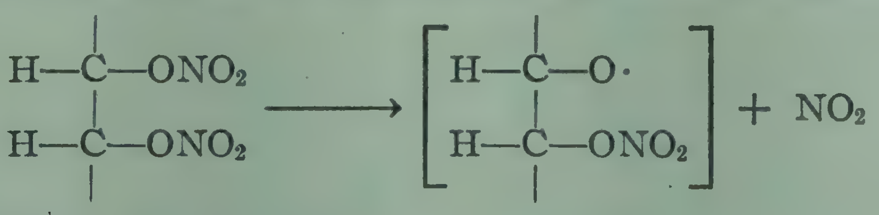


(17)



(18)

Acetone is produced by the decomposition, and the free methyl radical disappears by recombining to form ethane or by further reaction with other materials present in the reaction system. Extending these observations to the case of nitric esters leads to the following reaction sequence[45]:



(19)

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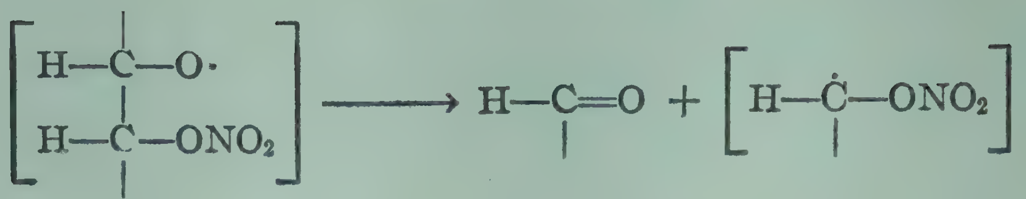
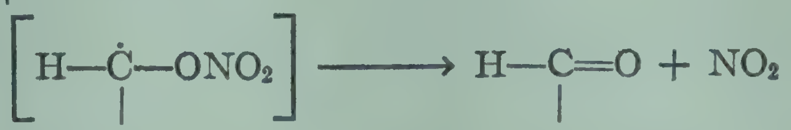
[45] L. Phillips, *Nature,* **160,** 753 (1947).



$$\left[\begin{array}{l} H-\overset{|}{C}-O\cdot \\ H-\underset{|}{C}-ONO_2 \end{array}\right] \longrightarrow H-\underset{|}{C}=O + \left[H-\underset{|}{\dot{C}}-ONO_2\right] \qquad (20)$$



$$\left[H-\underset{|}{\dot{C}}-ONO_2\right] \longrightarrow H-\underset{|}{C}=O + NO_2 \qquad (21)$$

The organic free radical formed in reaction 19 has the same general structure as that obtained from *tert*-butyl peroxide and is many times more reactive than the NO_2 also formed. The reactivity is such that all these processes occur simultaneously to bring about carbon–carbon bond cleavage and the production of aldehydes or ketones. It is possible that the free radicals will dehydrogenate other organic matter to produce alcohols, or they may add to unsaturated compounds.

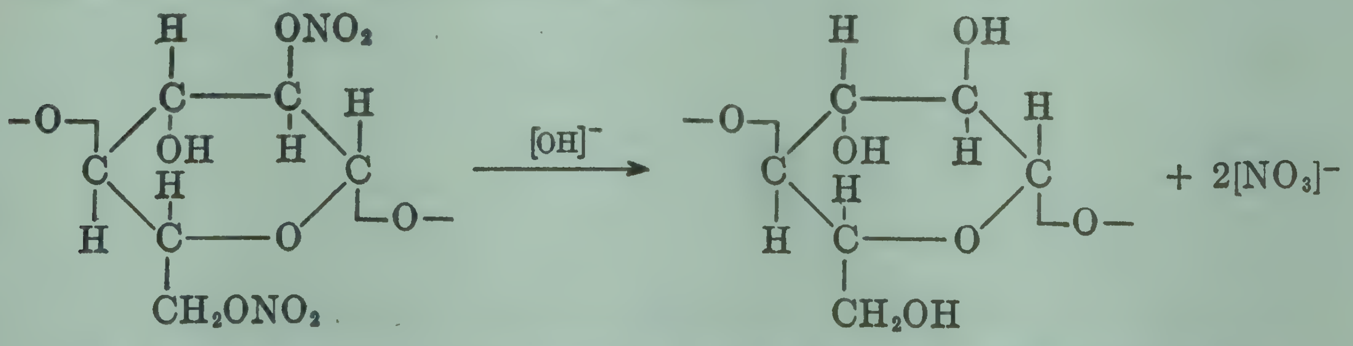
The cleavage reaction results in a rapid lowering of chain length, and the addition reaction can result in cross-linking with subsequent insolubilization in some systems. This spontaneous decomposition is not amenable to inhibition, and will progress in the case of cellulose nitrate at the rate of about 1% per hour at 135°C. Reduction in temperature is effective in slowing down the decomposition so that at room temperature degradation is negligible. As in the case of hydroperoxides, many substances are capable of accelerating the rate of degradation of cellulose nitrate. These include easily reducible materials such as aldehydes, as well as acids and bases.

Lucas and Hammett[46] have studied the base-catalyzed decomposition of benzyl nitrate and have shown that two first-order reactions are occurring:

$$C_6H_5CH_2ONO_2 \xrightarrow{[OH]^-} C_6H_5CH_2OH + [NO_3]^- \qquad (22)$$

$$C_6H_5CH_2ONO_2 \xrightarrow{[OH]^-} C_6H_5CHO + [NO_2]^- + H_2O \qquad (23)$$

It is an interesting speculation to extrapolate these findings to the case of cellulose nitrate, and from them to develop a possible mechanism for the base-catalyzed degradation reaction. Rewriting these two equations for cellulose nitrate leads to the following:



(24)

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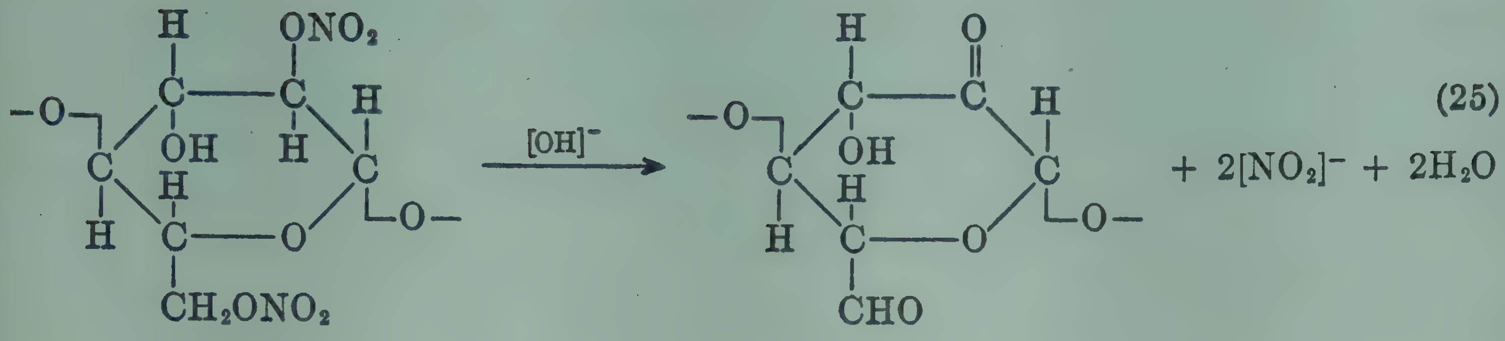
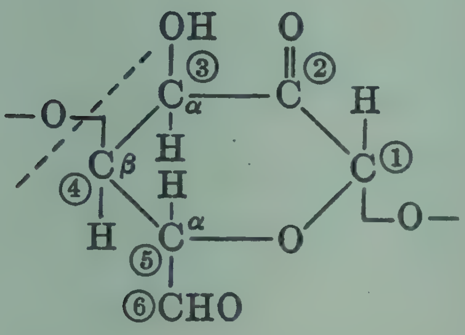
[46] G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, **64**, 1928 (1942).

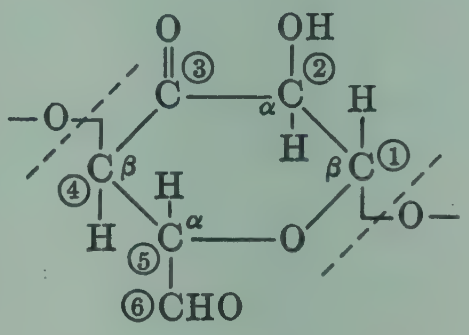


(25)

Reaction 24 is the simple ester hydrolysis reaction and would be expected to be nondegrading, since the acid formed would be neutralized by the hydrolyzing base. Reaction 25, on the other hand, could result in the production of an aldehyde group at the 6- position, a ketone group at the 2- or 3- position, or both. Such a compound would then be extremely sensitive to alkaline cleavage according to the mechanism discussed in Chapter III-C-3. Chain scission would occur as shown:



A. Ketone at carbon atom 2



B. Ketone at carbon atom 3

In the case A where an aldehyde group is present at position 6 and a ketonic group at 2, they are both in the beta configuration to the 4-glucosidic bond and would doubly enhance the alkali sensitivity of that glucosidic link. In the other case, B, the ketonic group is beta to the 1-glucosidic linkage and the aldehyde is beta to the 4-glucosidic bond; thus, both chain bonds are made alkali labile and will cleave so that the oxidized glucose unit is effectively chopped out of the chain. It is a distinct possibility that the mechanism of attack by the hydroxyl ion in these hydrolyses involves the hydrogen atom on the carbon atom attached to the nitric ester group. This attack would quite likely result in activating the β-glucosidic linkage toward alkaline cleavage without first requiring the conversion of the ester group to either aldehyde or ketone. In any event the actual cleavage mechanism would be the same, since it is the direct effect of beta activation by electronegative groups. The stabilization of cellulose nitrate has been exhaustively investigated, and a wide variety of compounds have been proposed for this purpose. Included in such a list are substances such as chalk, sodium silicate, or sodium carbonate,[47-50] ammonia,[51] petroleum jelly,[52-56] glucosides[57] containing unsaturates, phenanthrene,[56] tartaric and other polybasic acids,[58] amyl alcohol,[59,60] dimethylaniline,[60] dicyandiamide,[61] carbazole,[62-63] diphenylbenzidine,[64] and triphenylamine.[60] The effectiveness of most of these compounds depends upon their ability to consume NO_2 and HNO_3 by nitration reactions, forming inactive products. It should be noted that these stabilizers do not slow down the initial decomposition reaction of the nitrate; they simply prevent the occurrence of a self-accelerating reaction. Stabilizers of this type would not be expected to be effective unless the products of decomposition were NO_2 or HNO_3. It would be anticipated, therefore, that the presence or absence of air or oxygen would have a marked influence on the effectiveness of such substances, because of the necessity for oxidizing the volatile decomposition products to an absorbable state. Weak acids are added to neutralize small quantities of basic substances which might be present and which would bring about the alkaline cleavage discussed previously.

Commercial cellulose nitrate is commonly prepared by nitrating cellulose with mixed nitric and sulfuric acids, and as a result the initial product contains some bound sulfuric acid as its half-ester (see Section B of this Chapter IX). When present in the final product this group can hydrolyze off,

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[47] F. A. Abel, *Proc. Roy. Soc. (London)*, **15**, 417 (1867).

[48] Lenk, *Centralblatt, Neue Folge*, **9**, 906 (1864).

[49] Lenk, *Centralblatt, Neue Folge*, **11**, 570 (1866).

[50] T. H. Pelouze and Maurey, *Compt. rend.*, **59**, 363 (1864).

[51] R. E. Reeves and J. E. Giddens, *Ind. Eng. Chem.*, **39**, 1303, 1306 (1947).

[52] L. Monti, D. Dinelli, and F. Buni, *Gazz. chim. ital.*, **63**, 713 (1933); *Chem. Abstracts* **28**, 3903 (1934).

[53] M. Tonegutti, *Z. ges. Schiess- u. Sprengstoffw.*, **21**, 127 (1926); *Chem. Abstracts*, **21**, 1185 (1927).

[54] M. Tonegutti, *Ann. chim. applicata*, **22**, 620 (1932); *Chem. Abstracts*, **27**, 1176 (1933).

[55] M. Tonegutti, *Z. ges. Schiess- u. Sprengstoffw.*, **32**, 300 (1937); *Chem. Abstracts*, **32**, 1099 (1938).

[56] M. Tonegutti and E. Brandimarte, *Atti V congr. nazl. chim. pura applicata Rome*, **1935**, Pt. II, 916 (1936); *Chem. Abstracts*, **31**, 7649 (1937).

[57] R. Poggi, *Ann. chim. applicata*, **21**, 500 (1931); *Chem. Abstracts*, **26**, 1788 (1932).

[58] C. Krauz and A. Majrich, *Chem. Obzor*, **8**, 213 (1933); *Chem. Abstracts*, **28**, 4907 (1934).

[59] E. Berger, *Bull. soc. chim. France*, [4], **11**, 1049 (1912).

[60] M. Marqueyrol, *Mém. poudres*, **23**, 128, 158 (1928).

[61] J. Walter, *Z. angew. Chem.*, **24**, 62 (1911).

[62] C. E. Reese, U. S. Patent 1,358,653 (Nov. 9, 1921).

[63] R. Dalbert, *Mém. poudres*, **28**, 147 (1938).

[64] A. Douillet and H. Ficheroulle, *Mém. poudres*, **27**, 105 (1937).

giving sulfuric acid and initiating the autocatalytic decomposition outlined previously. One of the major problems of cellulose nitrate manufacture is therefore to eliminate even the slightest trace of bound sulfuric acid and to wash it out of the fiber. If the half-ester is not completely removed, some stabilization may be obtained by exactly neutralizing that which is retained. Extreme care should be taken when using such an expedient since an excess of base will activate the alkaline instability of the polymer.

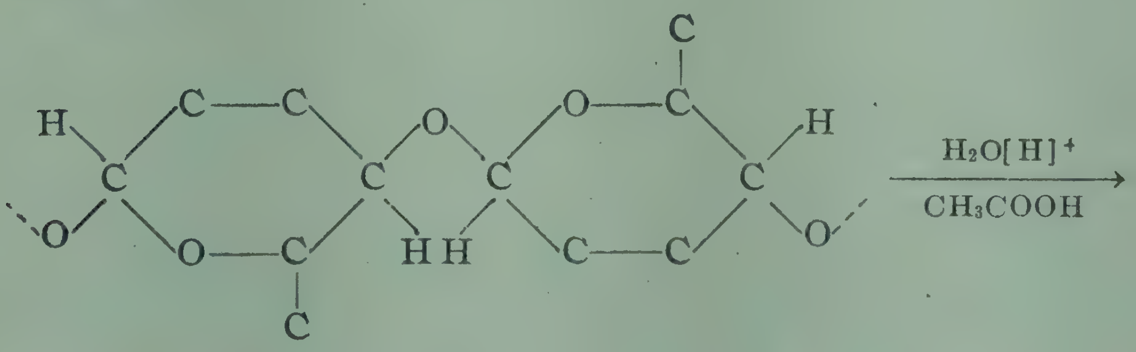
The stability characteristics of cellulose nitrate can be summarized by the following:

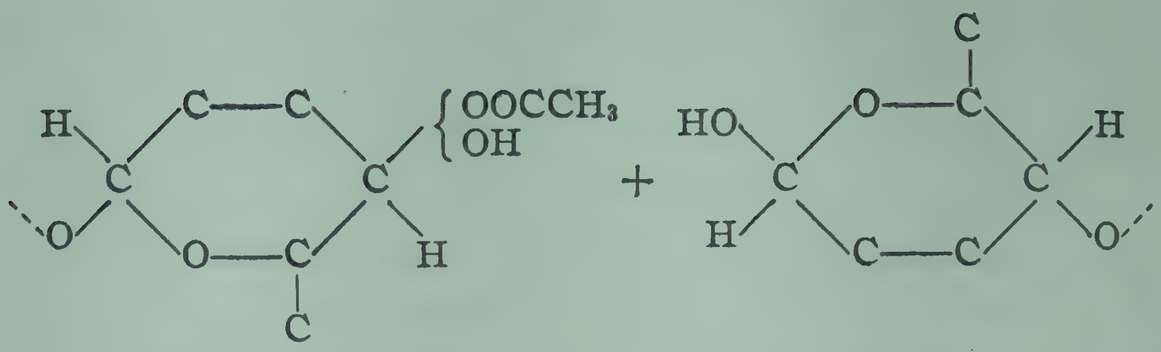
1. Thermal degradation of cellulose nitrate is a spontaneous reaction whose rate is temperature dependent and which cannot be prevented by antioxidants.
2. The products of decomposition, NO_2 and HNO_3, unless removed, will initiate a further autocatalytic phase of the decomposition.
3. The formation of carbonyl groups on the cellulose chain as a result of thermal denitration sensitizes the chain to alkaline cleavage.
4. Oxygen plays only a very minor part in the degradation of cellulose nitrate in contrast to its importance with the other cellulose derivatives.
5. Cellulose nitrate is subject to photochemical decomposition which is accelerated in air or oxygen.

(d) HYDROLYTIC DEGRADATION

Degradation of organosoluble cellulose derivatives by hydrolytic reaction can be attributed to acid cleavage of the glucosidic links in the polymer molecule, with the exception of the alkaline scission of cellulose nitrate discussed under the previous topic. The chain cleavage is accompanied by de-esterification with the esters and by de-etherification with the ethers. This reaction is of considerable importance in the manufacture of secondary cellulose acetates, where it is customary to utilize an acid-catalyzed homogeneous de-esterification reaction to convert the acetone-insoluble triester to an acetone-soluble derivative of lower D.S.

Under homogeneous conditions, depolymerization can occur either by acetolysis or by hydrolysis as illustrated in the accompanying reaction scheme:





In a homogeneous system containing both acetic acid and water, degradation will occur as a result of the medium effect (acetic acid hydrolysis) and can be greatly accelerated by the presence of strong acids such as sulfuric acid.[65] The reaction appears to obey the kinetic laws derived by af Ekenstam[66] for the random degradation of polymers and the rate of reaction is shown to be temperature dependent, increasing with temperature as would be anticipated. The reaction rates obtained by Hiller[65] are recorded in Table 49. From these data it is apparent that sulfuric acid accelerates the degradation to a marked degree.

TABLE 49

Reaction Rate Constants for Degradation of Cellulose Acetate (Hiller[65])

Temperature, °C.	Reaction rate constant × 10^6, hr.$^{-1}$
Uncatalyzed reaction	
84.4	0.77
94.2	2.1
104.4	8.1
115.1	20
Sulfuric acid-catalyzed reaction	
46.0	22
54.8	64
65.7	177

It is also of importance to compare the relative degradation tendency of cellulose acetate with its rate of deacetylation. Table 50 shows such a correlation from which several pertinent conclusions can be drawn.

The degradation occurring during this reaction has a larger activation energy[67] than does the deacetylation reaction. The degradative reaction is thus more temperature dependent than is the de-esterification; also, increases in reaction temperature will increase the extent of degradation

[65] L. A. Hiller, Jr., *J. Polymer Sci.*, **10**, 385 (1953).

[66] A. af Ekenstam, *Ber.*, **69B**, 549, 553 (1936).

[67] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.

obtained for a given change in degree of substitution. It is also interesting to observe that in the uncatalyzed reaction, the activation energy for deacetylating primary hydroxyls is much less than that required for secondary hydroxyls or for degradation. With sulfuric acid catalysis, however, the energy requirements for the hydrolysis of the secondary hydroxyls have been greatly reduced and the reaction appears to go faster than that of the primary hydroxyls.

TABLE 50

Energetics of Cellulose Acetate Deacetylation and Degradation (Hiller[65])

	Deacetylation		
Thermodynamic function Eyring notation[66]	Primary groups	Secondary groups	Degradation
Uncatalyzed reaction			
Experimental energy of activation, $E_{exptl.}$, kcal. mole^{-1}	14.3 ± 1.4	20.6 ± 0.4	29.6 ± 1.0
Heat of activation, $\Delta H^{\ddagger}$ (25° C.), kcal. mole^{-1}	13.7	20.0	29.0
Entropy of activation $\Delta S^{\ddagger}$ (25° C.), entropy units mole^{-1}	−39.2	−24.1	−12.6
Free energy of activation $\Delta F^{\ddagger}$ (25°C.), kcal. mole^{-1}	25.4	27.2	32.8
Sulfuric acid-catalyzed reaction			
Experimental energy of activation, $E_{exptl.}$, kcal. mole^{-1}	16.1 ± 5.8	8.5 ± 0.2	22.7 ± 2.0
Heat of activation, $\Delta H^{\ddagger}$ (25°C.), kcal. mole^{-1}	15.5	7.9	22.1
Entropy of activation, $\Delta S^{\ddagger}$ (25° C.), entropy units mole^{-1}	−29.6	−54.9	−17.7
Free energy of activation $\Delta F^{\ddagger}$ (25°C.), kcal. mole^{-1}	24.3	24.3	27.4

The loss in viscosity which organosoluble cellulose derivatives may undergo under acidic conditions is the direct consequence of the acid lability of the β-glucosidic bond joining the anhydroglucose units in the cellulose chain. It would be anticipated, therefore, that organosoluble esters and ethers of cellulose would be equally susceptible to acid degradation if they were exposed under conditions of a homogeneous reaction, where all of the β-glucosidic bonds would be equally available for attack. Experimental investigation has shown the above conclusion to be an oversimplification since it has neglected the possible role of the substituents in modifying the rate of cellulose chain cleavage under identical homogeneous reaction conditions.

Change in intrinsic viscosity versus time, as shown in Figure 91, was compared under identical acetolysis conditions for samples of ethyl cellulose, cellulose acetate, and cellulose nitrate.[68] It is apparent from the curves in Figure 91 that ethyl cellulose is the least stable and cellulose acetate the most stable, with cellulose nitrate occupying an intermediate position. The extreme difference in the rate of loss of intrinsic viscosity between ethyl cellulose and cellulose acetate is a striking example of how substituents can modify the basic characteristics of the cellulose molecule. Cellulose nitrate shows a somewhat ambiguous behavior which can be attributed to the complex nature of the denitration reaction.

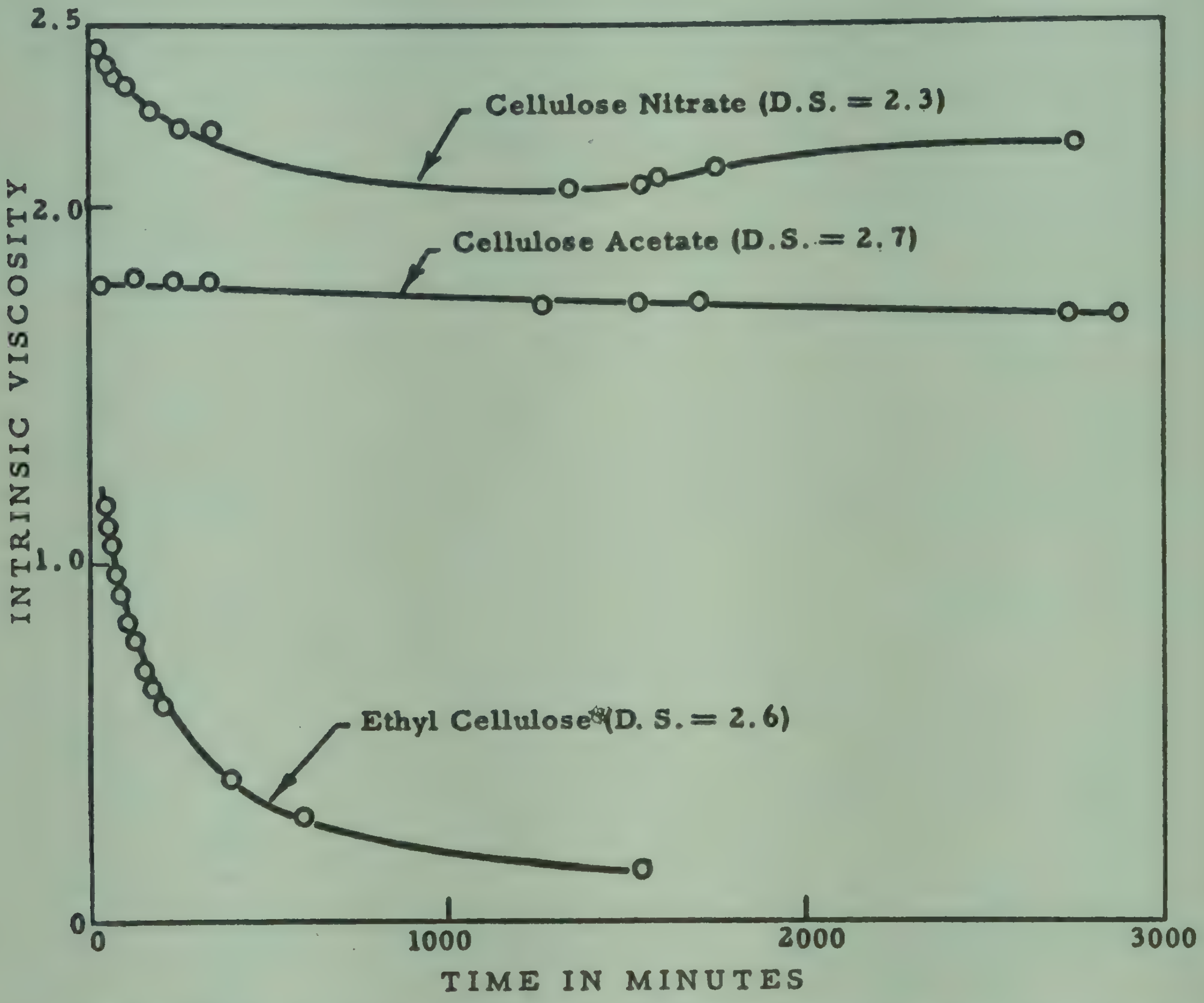


Fig. 91. Rates of acetolysis at 25°C. for ethyl cellulose, cellulose acetate, and cellulose nitrate (Lincoln, Reid, and McBurney[68]). Acetolysis was carried out in an anhydrous medium, 95:5 acetic acid:acetic anhydride which was 0.78 *N* with respect to HCl and 0.105 *N* with respect to LiCl.

Some attention in the literature has been directed toward the heterogeneous hydrolysis of cellulose acetate[69-71] and methyl cellulose.[72] The reaction in the case of methyl cellulose is very similar to the corresponding cellulose hydrolysis in that an initial rapid reaction is succeeded by a slow one, and the degradation appears to be tending toward a "leveling off" D.P. The conditions used with cellulose acetate resulted in deacetylation which was accompanied by a negligible amount of depolymerization.

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[68] D. C. Lincoln, A. R. Reid, and L. F. McBurney, unpublished results.

This discussion serves to point up a serious gap in our knowledge of cellulose derivative behavior, namely, the development of a sound theory to explain the substituent effect on the hydrolytic sensitivity of such compounds. It would be of great help to understand the effect of substituent size, polarity, extent of substitution, and uniformity of substitution on the activation energy and frequency factor in these cases.

[69] F. S. Sherman and I. O. Gol'dman, *J. Applied Chem.* (*U.S.S.R.*), **25** (English trans.), 87 (1952); *Chem. Abstracts*, **46**, 5836 (1952).

[70] E. Elöd and A. Schrodt, *Z. angew. Chem.*, **44**, 933 (1931).

[71] I. Sakurada and T. Morita, *J. Soc. Chem. Ind., Japan*, **41**, Suppl. binding, 385 (1938).

[72] R. Steele and E. Pacsu, *Textile Research J.*, **19**, 771 (1949).

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2.7.81	2.7.81		
17.7.81	17.7.81		
1.8.81	3.8.81		
18.8.81	17-8-81		
6.11.84	26.10.84		
12/9/91	20/4/92		
19/1/99	11/1/99		

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